STUDIES ON THE INTERACTION OF MICELLES WITH PESTICIDES

ABSTRACT

THESIS

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BY

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Abstract

Pesticide is a substance or mixture of substances indented for preventing, destroying, repelling or mitigating the pests.[1] Chemical pesticides may be classified into different groups namely insecticides, herbicides, fungicides, miticides, plant growth regulators, wood preservatives etc. They may be divided into two broad categories; Inorganic and Organic.

Commonly known inorganic pesticides are yellow phosphorus, sodium fluoride, lime sulfur, boric acid, mercuric chloride etc.

The organic pesticides includes natural or synthetic compounds. They can be divided into the following classes on the basis of their functional group:

Organochlorines: *Examples:* Dichloro diphenyl trichloroethane (DDT), benzene hexachloride (BHC), endosulfan, aldrin and heptachlor.

Organophosphates: *Examples:* Diazinon, malathion, parathion and paraxon.

Carbamates: *Examples:* Carbaryl, carbofuron and propoxur.

Carboxalic acid Derivatives: It includes, 2,4-dichlorophenoxy acetic acid (2,4-D), 2,4,5-trichlorophenoxy acetic acid (2,4,5-T), silvex and paraquat.

Triazines: It includes simazine and atrazine.

Phenylureas: These are the derivative of phenylurea, examples; isoproturon, fenuron, diuron and metaxuron

Pyrethroids: Pyrethroids are synthetic derivatives of pyrethrin. Cypermethrin and deltamethrin are good examples of synthetic pyrethroids.

Others: It includes thiocyanates, dinitorphenols, formamides organometallics.

Pesticides are available in various formulations[2,3] i.e., combination of the active ingredient with one or more inert substances. Pesticides are formulated to improve their characterstics such as handling, persistence on foliage, safety, and ability to mix with water. The different formulation are dusts, sprays, wettable powders, flowables, emulsifiable concentrates (EC), granules and encapsulated pesticides. EC occupies the most distinct place. The surfactants used in formulations help to increase the uptake of chemicals and is easy to apply. Surfactants also help to (i) increase the solubility of the pesticide/herbicide[4] in aqueous medium, (ii) stabilize the pesticide by controlling evaporation or decomposition (above cmc), (iii) enhance the effectiveness of the pesticide by providing the fine spray and (iv) explore the mode of action of the pesticide (hydrolysis behaviour) in biomacromolecular ensembles (e.g., enzymes).

Chemical reactivity in colloidal self-assemblies (e.g., micelles microemulsions, droplets and visicles) has got importance owning to similarities in action with the enzymatic reactions.[5] The structures of both micelles and enzymes are similar in that they have hydrophobic cores with polar groups on their surfaces. Both micelles and enzyme bind substrates in a

non-covalent manner. The kinetics of micellar catalysis resembles to that of enzymatic catalysis in which the micelles may be saturated by the substrate and conversely the substrate may be saturated by the micelle.

The phenylureas are widely used in agriculture as active principles of efficient herbicides.[6] They are absorbed by roots and leaves with translocation, and act as photosynthetic electron transport inhibitors upon the photosystem II.[7,8] Laudien and Mitzner[9,10] studied the kinetics and mechanism of the hydrolytic decomposition of a number of phenylureas in acidic and alkaline media. The kinetic and mechanistic aspects of the acidic and alkaline hydrolysis have also been investigated by other workers[11-14] under different conditions. Detailed micellar effect on acidic and alkaline hydrolysis of phenylureas have, however not been studied. The present work has been made to systematically study the kinetics of hydrolysis of phenylurea in micellar media of CTAB and NaLS. The aim of work also includes the influence of $[H^+]$,$[OH^-]$,[surfactant] and temperature on the rate of hydrolytic reaction of phenylureas. The study will be helpful in understanding the mechanism of action of herbicides in biological processes and also in predicting the fate of herbicide after its dispersal in the environment.

The work described in the thesis entitled **"Studies on the Interaction of Micelles with Pesticides"** deals with kinetic studies on the hydrolysis of isoproturon and fenuron in acidic and alkaline media, in the absence and presence of surfactants.

The thesis has been divided into four chapters, namely (i) Chapter-1; General Introduction, (ii) Chapter-2; Experimental, (iii) Chapter-3; Kinetics of acidic hydrolysis of phenylureas in CTAB and NaLS micelles, and (iv) Chapter-4; Kinetics of alkaline hydrolysis of phenylureas in CTAB and NaLS micelles.

Chapter-1 comprises of an introduction on pesticides, surfactants and micellar organization, kinetic treatment of reactivities in micellar systems and hydrolysis of phenylureas. The chapter ends with the statement of the problem, which suggests the importance of this study.

Chapter-2 describes the experimental details. The materials used, their structure and formulas, sources and purities are given along with the method of preparation of solution. Details of kinetic measurement are also given in this chapter.

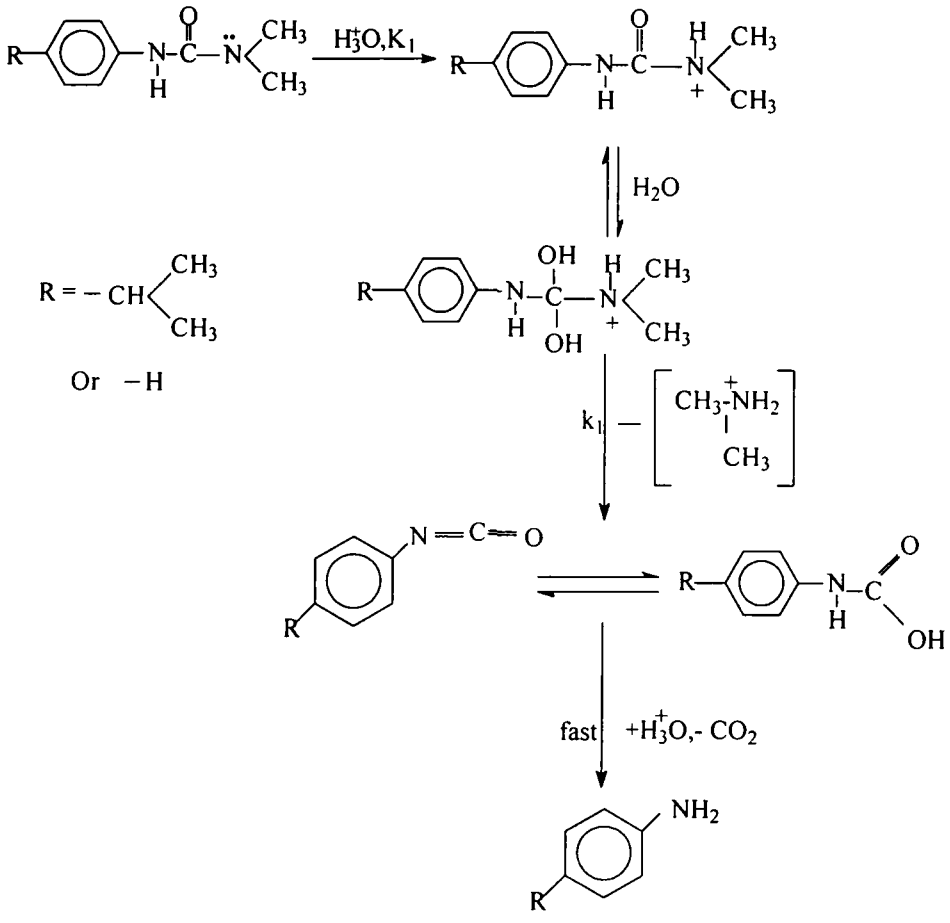
Chapter-3 describes the kinetics of acidic hydrolysis of phenylureas in aqueous and in presence of CTAB and NaLS micelles. Results cover all the observations obtained under varying conditions of temperature and concentrations of reactants, surfactants and salt. The discussion includes the interpretation of observed data.

Chapter-4 describes the kinetics of alkaline hydrolysis of phenylureas in aqueous and micellar media of CTAB and NaLS. Results and discussion cover the results obtained during various kinetic experiments and their interpretation.

The experiments performed at various initial [phenylurea] suggest that the reaction follows first-order kinetics

in [phenylurea] in both aqueous and micellar media (Figures 1-2). The rate of reaction initially increased with increasing [HCl], but at higher [HCl], the values of rate constant become independent of [HCl] (Figures 3-4).

The hydrolysis of phenylurea in the acidic medium is initiated by the protonation of amino group. The protonated phenylurea is then attacked by water (which is a rate determining step) to give tetrahedral intermediate. The tetrahedral intermediate decompose to yield phenyl isocyanate and corresponding amine (Scheme 1).

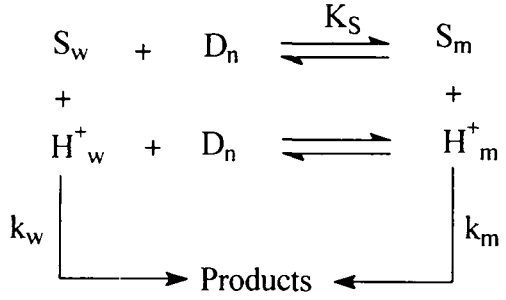


Scheme 1

Phenyl isocyanate is unstable in acidic medium and hydrolyze to give an another intermediate (i.e., phenyl carbamic acid) with a half life period of 20s[15] in acidic or neutral solution at 25°C. In acidic solution, phenyl carbamic acid is very unstable and decarboxylate rapidly to give finally the substituted aniline.

In low acidities, the concentration of the N-protonated phenylurea increases with the increase in acidities and reaches to maximum. Any further increase in concentration of HCl causes decrease in concentration of N-protonated phenylurea and favours the O-protonation. Giffney and Connor[16] concluded that N-protonated urea is the reactive entity while O-protonated conjugated acid does not decompose at low to intermediate acidities.

The similar behaviour in the dependence of the values of rate constants on [phenylurea] and [HCl] in aqueous and micellar media suggests that the same mechanism has been followed with all possible intermediate situations. The observed increase in the rate of acidic hydrolysis of phenylurea upon addition of NaLS micelles can be explained on the basis of pseudophase kinetic model presented by Scheme 2



Scheme 2

In this scheme 'S' denotes phenylurea, D_n is the micellized surfactant (i.e., $[D_n]$ = [Total surfactant] – cmc) and K_S is the binding constant of phenylurea with NaLS micelles, Subscript w and m denotes aqueous and micellar pseudophases, respectively.

Corresponding to the Scheme 2 the overall rate constant is given by:

$$k_\psi = \frac{k_w[H_T^+] + (k_m K_s - k_w) m_{H^+}[D_n]}{1 + K_s [D_n]} \qquad (1)$$

Where k_m and k_w are second-order rate constants for reaction in micellar and aqueous pseudophases, respectively. m_H^+ in terms of $[H_w^+]$, $[Na_T^+]$, $[D_n]$ and β can be expressed by:

$$(m_{H^+})^2 + \left(\frac{[Na_T^+] + [H_w^+]}{[D_n]} - \beta\right) m_{H^+} - \frac{\beta[H_w^+]}{[D_n]} = 0 \qquad (2)$$

Where β is the degree of binding of counter ion by the micellar surface.

The fitting value of k_m, K_{H^+/Na^+} and K_S were obtained from the computer program by minimizing the deviation between the simulation and the observed value for k_ψ - [surfactant] profile. The values of these parameters are given in Table 1. The rate enhancement of bimolecular reactions is ascribed largely to increase in concentration of reactants in the small volume of the association colloids. Addition of surfactant lead to binding of both reactants to micelles and thus increases the overall reaction rate.

A continuous inhibition in the rate of hydrolysis was observed in presence of CTAB micelles. The inhibition of

bimolecular reactions can be explained in terms of incorporation of organic substrate and exclusion of reactive H^+ ion. The hydrolysis is not completely suppressed in CTAB micelles because of the presence of very small concentrations of H^+ and N-protonated phenylurea at the micellar surface as co-ions. The concentration gradient of co-ions between water and the interface region is very large with dilute co-ions, but it decreases as total concentration is increased. Thus, under the condition of high concentration of co-ions, the concentration gradients disappear between the aqueous and the interfacial region and the inhibition reaction is decreased significantly as the total co-ions concentration is increased.

The residual hydrolysis of phenylureas by HCl at micellar surface of CTAB is considered to be very small and negligible. Therefore, the terms k_m and m_{H^+} in equation (1) is neglected and the rate equation takes the form of:

$$k_\psi = \frac{k_w [H_T^+]}{1 + K_S [D_n]} \qquad (3)$$

On inverting equation (3), we get:

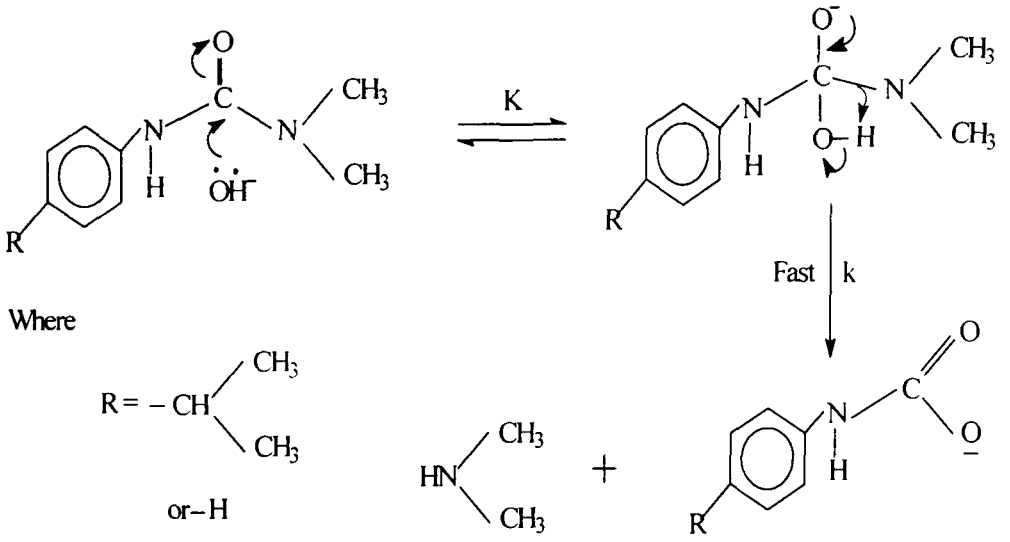
$$\frac{k_w [H_T^+]}{k_\psi} = 1 + K_S [D_n] \qquad (4)$$

A plot of $\frac{k_w [H_T^+]}{k_\psi}$ versus $[D_n]$ (Figure 5) gave a straight line.

The kinetic studies on alkaline hydrolysis of isoproturon and fenuron were performed in the aqueous and in micellar media of CTAB and NaLS. From the observed results it is evident that,

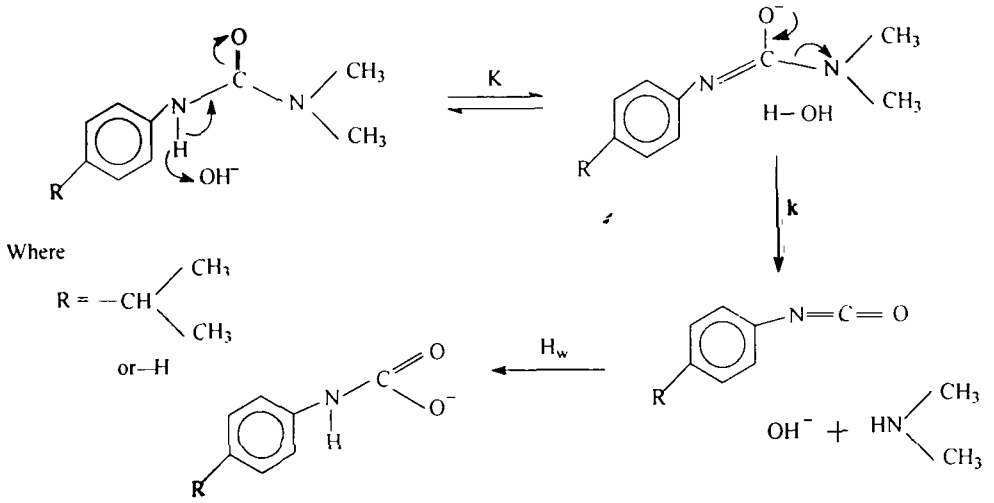
the reaction followed first-order kinetics with respect to [phenylurea] in both aqueous and micellar media (Figures 6-7). The order of the reaction in [NaOH] is fractional (Figures 8-9).

The attack of OH^- on the carbonyl carbon initiates the hydrolysis of phenylurea. It form intermediate hydroxide ion addition complex. Water acting as general acid, protonates the intermediate to facilitate the elimination of dimethylamine along with the formation of carbamate. Thus, the reaction proceeds through an addition-elimination mechanism as presented in Scheme 3.



Scheme 3

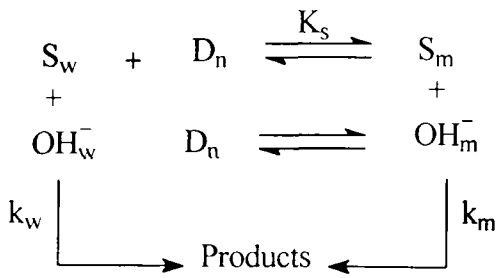
In stronger basic media, the reaction is initiated by the formation of conjugate base of phenylurea caused by deprotonation of the aryl-NH-group as presented in Scheme 4.



Scheme 4

In this mechanism the rate determining step is the elimination of dimethyl amine from the anion of phenylurea to give phenyl isocyanate. The phenyl isocyanate, then react rapidly either with water or at pH > 8 with hydroxide ion to give carbamate. At pH > 10, the carbamate is relatively long lived. In the acidic and neutral media the carbamate decarboxylates rapidly to yield corresponding aniline. With the increase in basicity, the activity of water decreases and, therefore, the rate of hydrolysis becomes constant.

The alkaline hydrolysis of phenylurea occurring in CTAB micelles can be presented by Scheme 5.



Scheme 5

The corresponding rate constant is given by:

$$k_{\psi} = \frac{k_w [OH_T^-] + (k_m K_S - k_w) m_{OH^-} [D_n]}{1 + K_S [D_n]} \quad (5)$$

m_{OH^-} can be expressed by the following quadratic equation

$$m_{OH}^2 + m_{OH} \left[\frac{[OH_T^-] + K_{OH^-/Br^-} [Br_T^-]}{(K_{OH^-/Br^-} - 1)[Dn]} - \beta \right] - \frac{\beta [OH_T^-]}{(K_{OH^-/Br^-} - 1)[D_n]} = 0 \quad (6)$$

where β is the fraction of neutralized micellar surface. The values of k_m, K_S and K_{OH^-/Br^-} obtained from the simulation of k_{ψ}- [surfactant] profile are given in Table 2.

The plot of k_{ψ} versus [CTAB] shows a peaked behaviour in which the maximum rate is obtained at [CTAB] ($\approx 2.0 \times 10^{-2}$ mol dm^{-3} for isoproturon) and ($= 1.0 \times 10^{-2}$ mol dm^{-3} for fenuron). The rate of hydrolysis decreases on further increasing the [CTAB]. The observed higher rate in CTAB micelles could be attributed to the binding of phenylurea on the positively charged micellar surface. The electron rich carbonyl part of phenylurea may be oriented towards the positively charged surface of CTAB micelles. Thus, the OH^- and reactive group of phenylurea lie in the Stern's layer and the reaction catalyzed by CTAB micelles mainly occur in this Stern's layer.

The decrease in rate of hydrolysis at higher CTAB concentration may be due to dilution of $[OH^-]$ in micellar phase, as the number of micelles increases. The other factor, which contribute towards the decrease in rate constants is the displacement of OH^- by unreactive Br^- from the vicinity of Stern's layer.

A continuous decrease in the values of rate constant was observed with increase in [NaLS]. The inhibition of the reaction is explained by considering the fact that OH^- being anionic does not bind to NaLS micelles. The deprotonated phenylurea or negatively charged tetrahedral intermediate is also being repelled by NaLS micelles. The rate constant for reaction occurring in presence of NaLS is given by:

$$k_\psi = \frac{k_w[OH^-_T]}{1 + K_s[D_n]} \qquad (7)$$

Which on inverting gives equation (8)

$$\frac{k_w[OH^-_T]}{k_\psi} = 1 + K_s[D_n] \qquad (8)$$

A straight line obtained (Figure 5) for the plot of $\frac{k_w[OH^-_T]}{k_\psi}$ versus $[D_n]$ gave the value of K_s.

The effect of temperature on the rate constant for the acidic and alkaline hydrolysis of phenylurea in presence of surfactants was used to evaluate activation parameters and are presented in Tables 3-4. The decrease in entropy of the reaction in the presence of micelles suggests that the reactants are in greater degree of orderliness while an increase in entropy shows greater degree of randomness. The addition of NaCl and KNO_3 decreased of rate of acidic and alkaline hydrolysis of phenylurea in the micellar media. The presence of salt displaces the reactants from the Stern's layer and also affect the micellar shape and size [17-18].

Table. 1

Values of rate parameters used to simulate k_ψ - [surfactant] profile and binding constant for the acidic hydrolysis of phenylureas (isoproturon and fenuron) in NaLS and CTAB micelles.

Reaction conditions:

[Phenylureas] = 5.0×10^{-5} mol dm^{-3}

[HCl] = 0.1 mol dm^{-3}

Parameters and Constants	Values			
	Isoproturon (at 70°C)		Fenuron (at 80°C)	
	in NaLS	in CTAB	in NaLS	in CTAB
K_s (mol^{-1} dm^3)	410.00	24.31	400.00	28.82
k_m (mol^{-1} dm^3 s^{-1})	$2.43 \pm 0.19 \times 10^{-4}$	-	$1.41 \pm 0.11 \times 10^{-4}$	-
β	0.75	-	0.75	-
K_{H^+/Na^+}	1.00	-	1.00	-
cmc (mol dm^{-3})	8.36×10^{-3}	8.02×10^{-4}	8.64×10^{-3}	8.52×10^{-4}

Table. 2

Values of rate parameters used to simulate k_{ψ} - [surfactant] profile and binding constant for the alkaline hydrolysis of phenylureas (isoproturon and fenuron) in NaLS and CTAB micelles.

Reaction conditions:

[Phenylurea] = 5.0×10^{-5} mol dm^{-3}

[NaOH] = 0.1 mol dm^{-3}

Parameters and Constants	Values			
	Isoproturon (at 70°C)		Fenuron (at 80°C)	
	in NaLS	in CTAB	in NaLS	in CTAB
K_s (mol^{-1} dm^3)	10.21	240.00	18.00	220.00
k_m (mol^{-1} dm^3 s^{-1})	-	$1.43 \pm 0.26 \times 10^{-4}$	-	$1.52 \pm 0.24 \times 10^{-4}$
β	-	0.80	-	0.80
K_{OH^-/Br^-}	-	6.00	-	6.00
cmc (mol dm^{-3})	8.32×10^{-3}	8.04×10^{-4}	8.61×10^{-3}	8.26×10^{-4}

Table. 3

Values of activation parameters for the hydrolysis of phenylureas (isoproturon and fenuron) in the aqueous and in presence of CTAB and NaLS micelles by hydrochloric acid.

Reaction conditions:

[Phenylurea] = 5.0×10^{-5} mol dm^{-3}

[HCl] = 0.1 mol dm^{-3}

Activation Parameters	Isoproturon			Fenuron		
	in Aqueous	in CTAB	in NaLS	in Aqueous	in CTAB	in NaLS
E_a (kJ mol^{-1})	14.01 ±1.23	22.32 ±1.44	30.16 ±1.61	36.05 ±2.42	31.28 ±1.76	27.32 ±2.11
$\Delta H^{\#}$ (kJ mol^{-1})	11.53 ±1.62	19.85 ±1.10	27.67 ±1.74	33.58 ±2.51	28.81 ±2.12	24.84 ±1.68
$-\Delta S^{\#}$ (JK^{-1} mol^{-1})	284.01 ±4.01	219.07 ±5.32	225.06 ±6.00	215.87 ±6.30	234.25 ±4.26	242.56 ±8.81

[CTAB] = 2.0×10^{-2} mol dm^{-3} and [NaLS] = 2.0×10^{-2} mol dm^{-3} for isoproturon

[CTAB] = 1.0×10^{-2} mol dm^{-3} and [NaLS] = 1.0×10^{-2} mol dm^{-3} for fenuron.

Table. 4

Values of activation parameters for the hydrolysis of phenylureas (isoproturon and fenuron) in the aqueous and in presence of CTAB and NaLS micelles by sodium hydroxide.

Reaction conditions:

[Phenylurea] = 5.0×10^{-5} mol dm^{-3}

[NaOH] = 0.1 mol dm^{-3}

Activation Parameters	Isoproturon			Fenuron		
	in Aqueous	in CTAB	in NaLS	in Aqueous	in CTAB	in NaLS
E_a (kJ mol^{-1})	35.31 ±1.23	39.01 ±1.56	24.95 ±0.91	51.82 ±1.29	48.33 ±1.24	43.85 ±1.19
$\Delta H^{\#}$ (kJ mol^{-1})	32.83 ±1.02	36.53 ±1.43	22.47 ±0.82	49.34 ±1.43	45.87 ±1.36	41.34 ±1.39
$-\Delta S^{\#}$ (JK^{-1} mol^{-1})	233.53 ±4.68	219.56 ±4.41	266.45 ±5.01	223.56 ±4.01	235.24 ±4.36	250.41 ±4.68

[CTAB] = 2.0×10^{-2} mol dm^{-3} and [NaLS] = 2.0×10^{-2} mol dm^{-3} for isoproturon

[CTAB] = 1.0×10^{-2} mol dm^{-3} and [NaLS] = 1.0×10^{-2} mol dm^{-3} for fenuron.

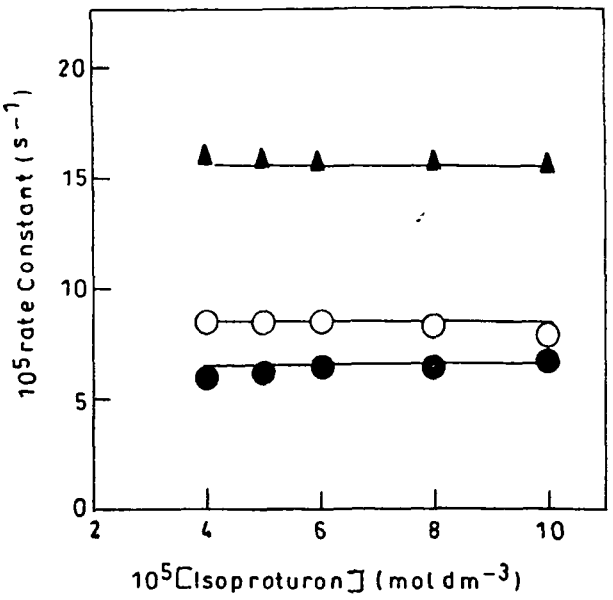


Figure 1 Effect of variation of [Isoproturon] on the values of rate constant in (o) aqueous, (•) CTAB and (▲) NaLS media.

Reaction Conditions: [HCl] = 0.1 mol dm^{-3}; [CTAB] =2.0×10^{-2} mol dm^{-3} and [NaLS] =2.0×10^{-2} mol dm^{-3} at 70°C.

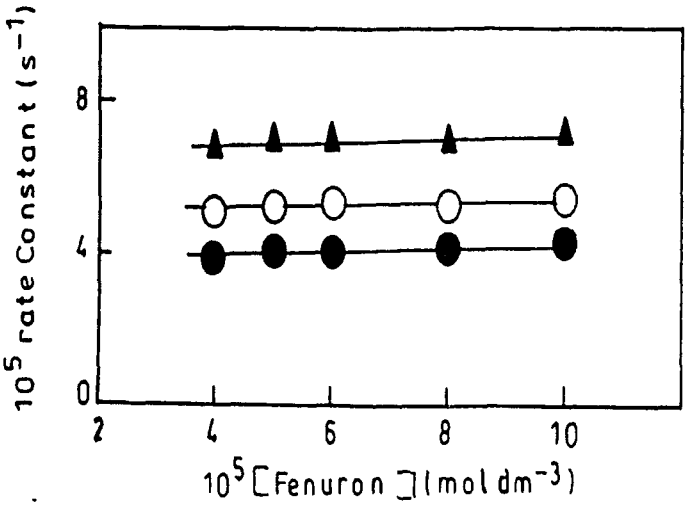


Figure 2 Effect of variation of [Fenuron] on the values of rate constant in (o) aqueous, (•) CTAB and (▲) NaLS media.

Reaction Conditions: [HCl] = 0.1 mol dm^{-3}; [CTAB] =1.0×10^{-2} mol dm^{-3} and [NaLS] =1.0×10^{-2} mol dm^{-3} at 80°C.

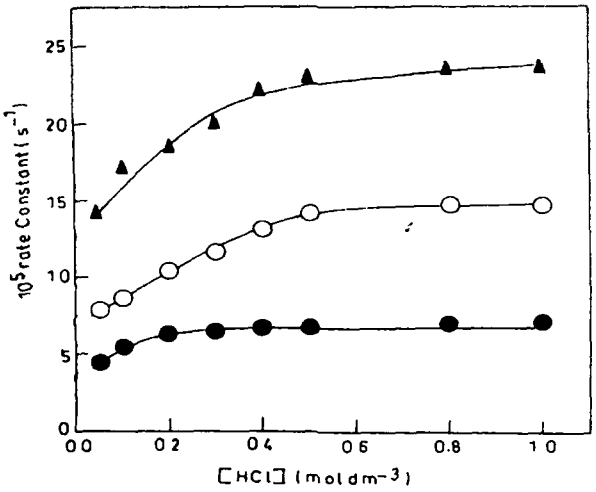


Figure 3 Effect of variation of [HCl] on the values of rate constant in (o) aqueous, (•) CTAB and (▲) NaLS media.

Reaction Conditions: [Isoproturon] = 5.0×10^{-5} mol dm^{-3}; [CTAB] =2.0×10^{-2} mol dm^{-3} and [NaLS] = 2.0×10^{-2} mol dm^{-3} at 70°C.

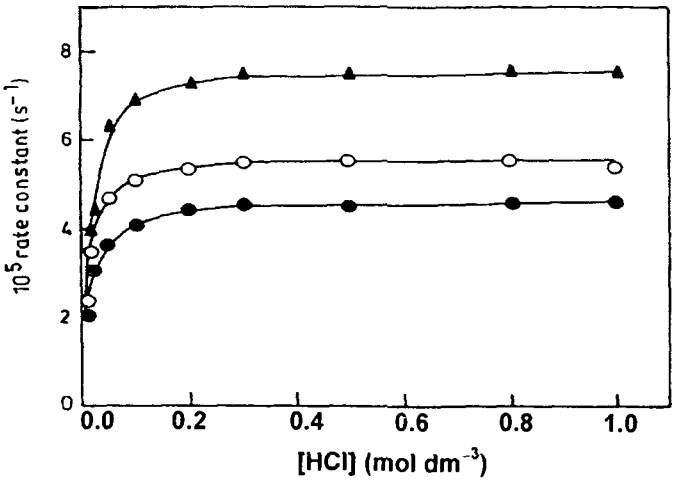


Figure 4 Effect of variation of [HCl] on the values of rate constant in (o) aqueous, (•) CTAB and (▲) NaLS media.

Reaction Conditions: [Fenuron] = 5.0×10^{-5} mol dm^{-3}; [CTAB] =1.0×10^{-2} mol dm^{-3}; and [NaLS] =1.0×10^{-2} mol dm^{-3} at 80°C.

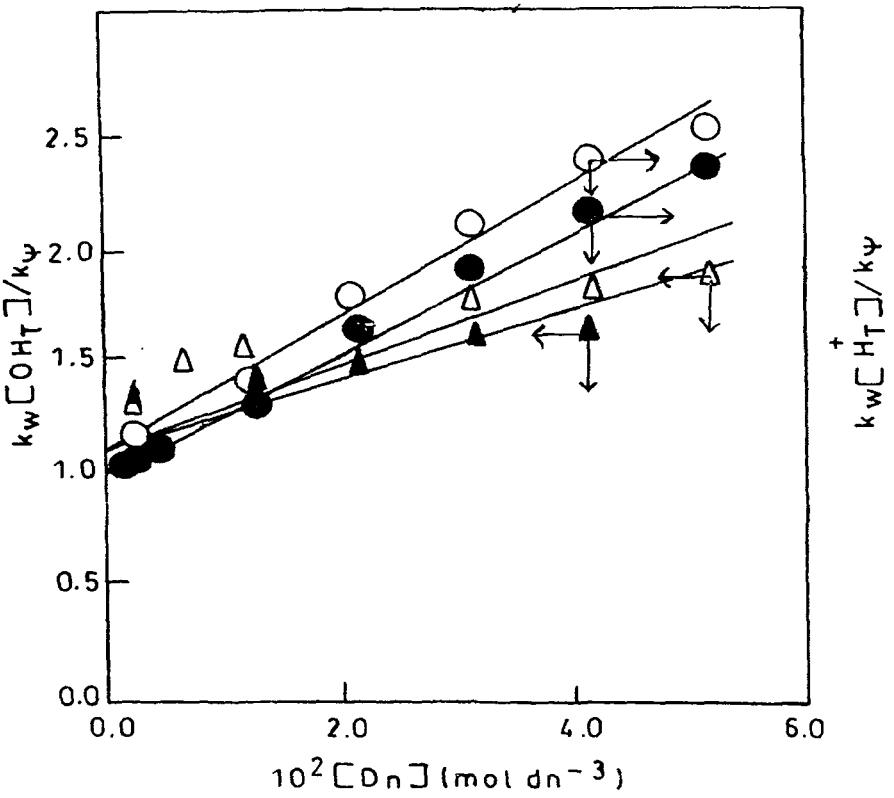


Figure 5 Plot of $\frac{k_w[OH_T^-]}{k_\psi}$ versus $[D_n]$ for the alkaline hydrolysis of (▲) isoproturon and (Δ) fenuron

Reaction Conditions: [phenylurea] = 5.0×10^{-5} mol dm^{-3} and [HCl] = 0.1 mol dm^{-3} at 70°C for isoproturon and 80°C for fenuron.

Plot of $\frac{k_w[H_T^+]}{k_\psi}$ versus $[D_n]$ for the acidic hydrolysis of (•) isoproturon and (o) fenuron

Reaction Conditions: [phenylurea] = 5.0×10^{-5} mol dm^{-3} and [NaOH] = 0.1 mol dm^{-3} at 70°C for isoproturon and 80°C for fenuron.

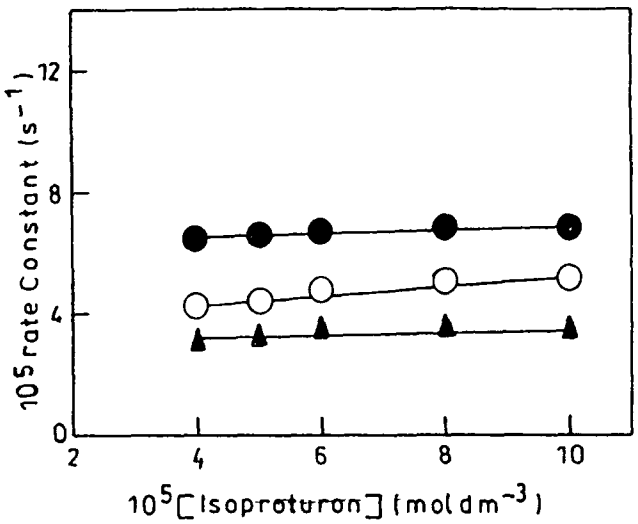


Figure 6 Effect of variation of [Isoproturon] on the values of rate constant in (o) aqueous, (•) CTAB and (▲) NaLS media.

Reaction Conditions: [NaOH] = 0.1 mol dm^{-3}; [CTAB] =2.0 × 10^{-2} mol dm^{-3} and [NaLS] =2.0×10^{-2} mol dm^{-3} at 70°C.

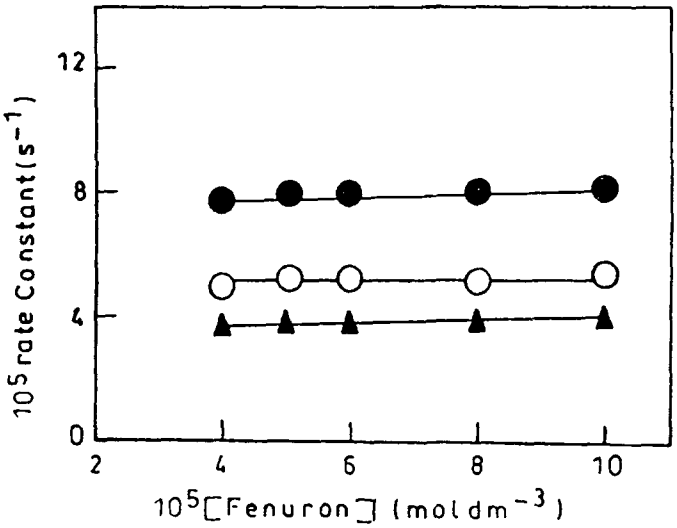


Figure 7 Effect of variation of [Fenuron] on the values of rate constant in (o) aqueous, (•) CTAB and (▲) NaLS media.

Reaction Conditions: [NaOH] = 0.1 mol dm^{-3}; [CTAB] =1.0 × 10^{-2} mol dm^{-3} and [NaLS] =1.0×10^{-2} mol dm^{-3} at 80°C.

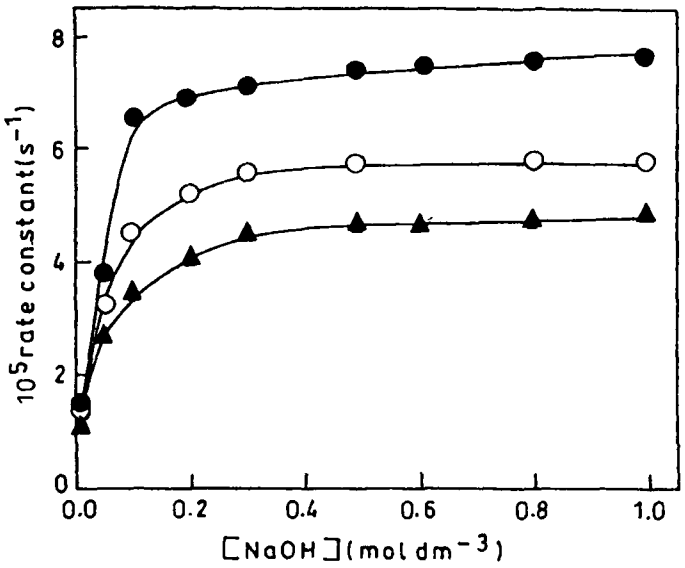


Figure 8 Effect of variation of [NaOH] on the values of rate constant in (o) aqueous, (•) CTAB and (▲) NaLS media.

Reaction Conditions: [Isoproturon] = 5.0×10^{-5} mol dm^{-3}; [CTAB] =2.0×10^{-2} mol dm^{-3} and [NaLS] =2.0×10^{-2} mol dm^{-3} at 70°C.

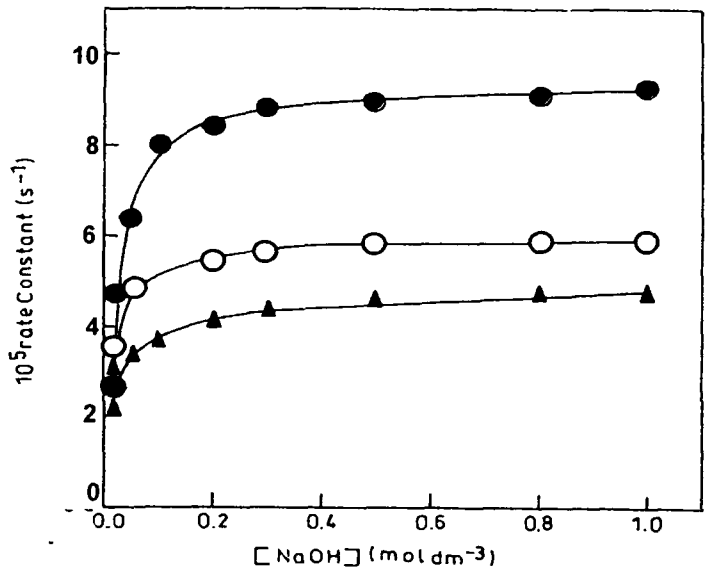


Figure 9 Effect of variation of [NaOH] on the values of rate constant in (o) aqueous, (•) CTAB and (▲) NaLS media.

Reaction Conditions: [Fenuron] = 5.0×10^{-5} mol dm^{-3}; [CTAB] =1.0×10^{-2} mol dm^{-3} and [NaLS] =1.0×10^{-2} mol dm^{-3} at 80°C.

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STUDIES ON THE INTERACTION OF MICELLES WITH PESTICIDES

THESIS

SUBMITTED FOR THE AWARD OF THE DEGREE OF

Doctor of Philosophy

IN

APPLIED CHEMISTRY

BY

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UNDER THE SUPERVISION OF

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2007

Dedicated

To

My Beloved Parents

DEPARTMENT OF APPLIED CHEMISTRY
FACULTY OF ENGINEERING & TECHNOLOGY
ALIGARH MUSLIM UNIVERSITY
ALIGARH-202002 (INDIA)

Dr. M.Z.A. Rafiquee
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Certificate

This is to certify that the thesis entitled ***"Studies on the Interaction of Micelles with Pesticides"*** submitted for the award of the degree of **Doctor of Philosophy in Applied Chemistry,** is a faithful record of the bonafide research work carried out at the Department of Applied Chemistry, Zakir Hussain College of Engineering and Technology, Aligarh Muslim University, Aligarh by **Mr. Santosh Kumar Gangwar** under my guidance and supervision.

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Supervisor

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S.K. Gangwar

(Santosh Kumar Gangwar)

LIST OF PUBLICATIONS

1. Polarographic study on parathion in micellar media.
   M.Z.A. Rafiquee, H.S. Rathore, S.K. Gangwar and Kabir-ud-Din
   J. Indian Chem. Soc., 82 (2005) 329-332.

2. Kinetics of the acid hydrolysis of isproturon in the absence and presence of sodium lauryl sulfate (NaLS) micelles.
   S.K. Gangwar and M.Z.A. Rafiquee, *Colloid and Polym. Sci.*, 285 (2007) 587-592.

3. Kinetics of the alkaline hydrolysis of isoproturon in CTAB and NaLS micelles.
   S.K. Gangwar and M.Z.A. Rafiquee, *Int. J. Chem. Kinet.*, 39 (2007) 39-45.

4. Kinetics of the acidic hydrolysis of fenuron in the aqueous and micellar media.
   S.K. Gangwar and M.Z.A. Rafiquee, *Colloid and Polym. Sci.*, (Communicated)

5. Kinetics of the alkaline hydrolysis of fenuron in the aqueous and micellar media.
   S.K. Gangwar and M.Z.A. Rafiquee, *Int. J. Chem. Kinet.*, (Communicated).

CONTENTS

CHAPTERS

Chapter-1

General Introduction

1.1 Pesticides and their Classification

A substance or mixture of substances indented for preventing, destroying, repelling or mitigating the pests is called pesticides.[1,2] Chemical pesticides, which are used on large scale in agriculture[3-5] may be classified into different groups namely insecticides, herbicides, fungicides, miticides, nematicides, plant growth regulators, wood preservatives etc. Insecticides are used to control insect pest such as caterpillar that feeds on crop and reduces yield. Herbicides control the growth of weeds that compete with crop for space, light and nutrients. Fungicides kill fungal disease that can cause toxicity in food. Miticides kill the mites and ticks while nematicides kill to the nematodes. Wood preservatives are used to kill the wood destroying organisms.

Chemical pesticides may be classified into two broad categories:

1.1.1 Inorganic pesticides

1.1.2 Organic pesticides

1.1.1 Inorganic Pesticides

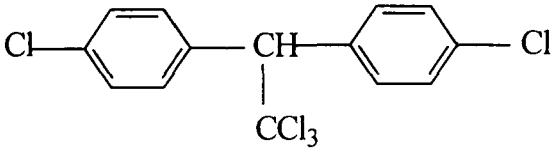
Commonly used inorganic pesticides are sodium fluoride, lime sulfur, boric acid, mercuric chloride, yellow phosphorus etc.

1.1.2 Organic Pesticides

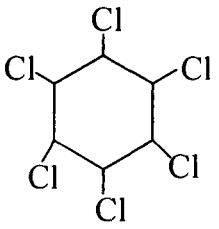
Organic pesticides can be either natural (often extracted from plants or bacteria) or synthetic. Most pesticides used today are synthetic organic chemicals. Organic pesticides can also be divided into the following broad classes on the basis of their functional group.

1.1.2.1 Organochlorines or Chlorinated Hydrocarbons

Dichloro diphenyl trichloroethane (DDT), benzene hexachloride (BHC), endosulfan, aldrin, heptachlor and chlordane are the pertinent examples of this type of pesticides. They are non-biodegradable and are persistent in the environment for a long period. They are readily soluble in lipids and even a low concentration of these pesticides may accumulate in the body fat of mammals that might pose problem in the long run. Organochlorine pesticides have a special significance in water as they are picked up by micro-organism mainly unicellular microorganism like zooplankton.



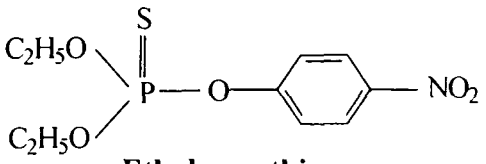
Dichloro diphenyl trichloroethane



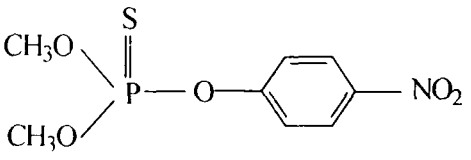
Benzene hexachloride

1.1.2.2 Organophosphates or Phosphorus Containing Pesticides

The organophosphates include diazinon, malathion, parathion and paraxon. More potent less persistent organophosphates have an advantage of having a non-lipophilic nature, moderate persistence and more potency than chlorinated pesticides. These pesticides affect the nervous system by disrupting the enzyme that regulates acetylcholine, a neurotransmitter. Most organophosphates are insecticides. They breakdown rapidly and usually are not persistent in the environment.



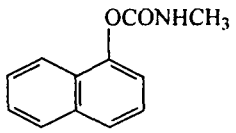
Ethyl parathion



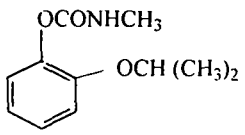
Methyl parathion

1.1.2.3 Carbamates

Commonly used carbamates are carbaryl, carbofuran, propoxur and sodium diethyldithiocarbamate(NaDDC). They are readily soluble in water and have reversible mode of action, less persistence, systemic nature and adequate potency against crop pests. These pesticides affect the system by disrupting an enzyme that regulates acetylcholine. The enzyme effect is usually reversible.



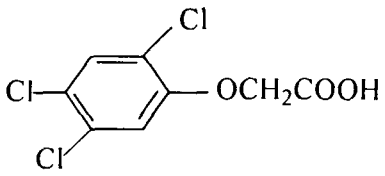
Carbaryl



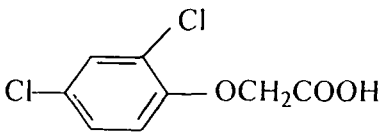
Propoxur

1.1.2.4 Carboxalic Acid Derivatives

These include 2,4,5-trichlorophenoxy acetic acid (2,4,5-T), silvex, Paraquat, 2,4-dichlorophenoxy acetic acid (2,4- D.) and diquat. They are considered as a potent source of environmental hazards, especially when their degradation products remain active in the environment after desired purpose is over. They are used as herbicides both on agriculture lands and in eradicating weeds in non-productive areas such as roadsides and electric transmission lines. In the aquatic environment the anaerobic micro-organism which often predominate are not always effective in degrading these pesticides.



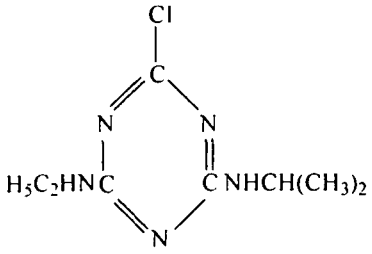
2,4,5-Trichlorophenoxy acetic acid



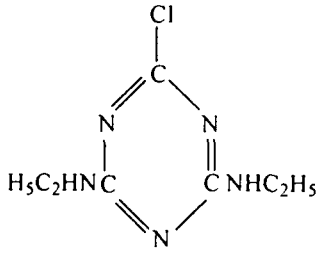
2,4-Dichlorophenoxy acetic acid

1.1.2.5 Triazines

They are derived from urea. The triazines such as atrazine and simazine are used in large quantities as a pre-emergent herbicide in cornfield. There is considerable persistence of the resulting products. In aerobic aqueous systems, including moist substitution of a hydroxyl group for the chlorine atom precedes ring cleavage and complete degradation.



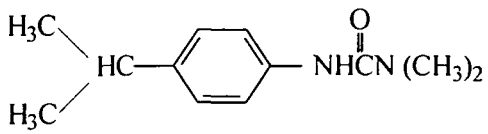
Atrazine



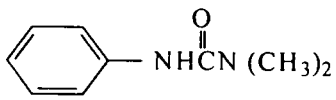
Simazine

1.1.2.6 Phenylureas

These are the derivatives of phenylurea e.g., diuron, metaxuron, isoproturon, fenuron and monuron. They are widely used for the control of different weed species in cereal and carrot. Some phenylureas are used to control woody plants and perennial plants.



Isoproturon

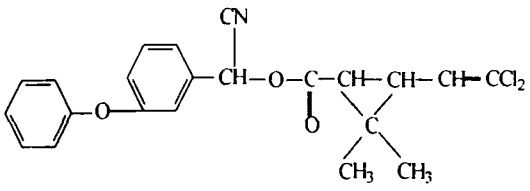


Fenuron

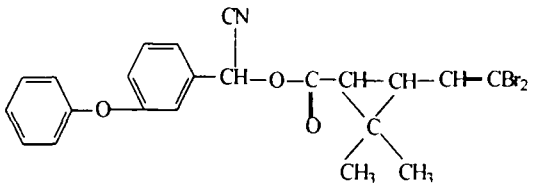
1.1.2.7 Pyrethroids

This class of compounds is related to pyrethrins, a naturally occurring insecticide. They are synthetic derivative of pyrethrin. They are obtained from plant chrysanthemums and are very stable in

sunlight. Some synthetic pyrethroids are toxic to the nervous system. Cypermethrin is good example of synthetic pyrethroids.



Cypermethrin



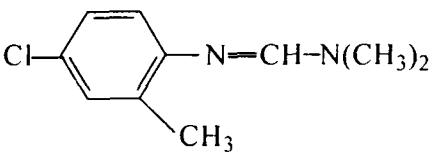
Deltamethrin

1.1.2.8 Neem products

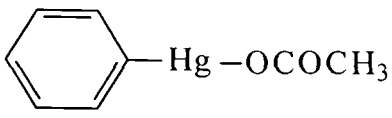
The limonoids present in neem tree and its products have made it useful insecticide, bactericide, fungicide, etc. Neem crudes such as its kernell crush and oil which are the potential source of bio-active action, can be formulated as ready to use dust and water dispersible powder and emulsifiable concentrate repetitively.

1.1.2.9 Others

It includes thiocyanates, dinitrophenols, formamides, organometallics etc. Thiocyanates have creosote like odour. They interfere with cellular respiration and metabolism. The nitrophenols have been used as avicides, insecticides, acaricides, fungicides and blossom thinning agents. The formamides comprise a very new, small, but promising group of insecticides. Its most important example is chlordimeform which is used to control the organophasphate and carbamate resistant pests. Their mode of action is the inhibition of enzyme monoamine oxidase.



Chlordimeform



Phenylmercury acetate

1.1.3 Formulation of Pesticides

Pesticides are useful chemicals and need a lot of caution and care during handling and application. Pesticides are available in various formulations.[6-8] The pesticide itself, or the ingredient which actually has the toxic action, is called the active ingredient. Pesticide formulation is a combination of the active ingredient and one or more inert ingredients. Inert ingredients usually are added to improve the effectiveness of the active ingredient. These inert ingredients usually determine the method of application.

Pesticides are formulated in various ways to improve such characteristics as handling, persistence on foliage, safety, ease of application and ability to mix with water. There are many different formulation types. The most important formulations are described as follows:

1.1.3.1 Dusts

Dusts are dry materials that are made by the combination of the active ingredient with an inert material that act as a diluent or carrier. Dust usually contain one to five percent active ingredient and is designed for dry application. Dust formulation has lost popularity, because of equipment difficulties, excessive drift and applicator inhalation hazard.

1.1.3.2 Sprays

Sprays are materials in which active ingredients are formulated as a liquid solution. Emulsifying additive is needed for water insoluble active ingredients.

1.1.3.3 Wettable Powder

For an active ingredient insoluble in water, the pesticide may be formulated as a wettable powder. The active ingredient in a wettable power is combined with a solid material- usually a clay or talc and suspended in water- with the aid of an emulsifier. These formulations require vigorous and continuous agitation during application. They may also pose increased hazard during mixing because they can be easily inhaled during mixing.

1.1.3.4 Dry Flowables or Water Dispersible Granules

Flowables are formulated by impregnating the active ingredient on a diluent or carrier, such as clay or talc. These formulations have replaced many wettable powders due to increased ease of handling and reduced hazard during mixing. Flowable formulations are used with pesticide that can be produced only in solid or semi solid form.

1.1.3.5 Emulsifiable Concentrates

The emulsifiers are surface-active agent that promote mixing with water to form a suspension. When an emulsifier is added to the active ingredient it is usually called an emulsifiable concentrate. Emulsifiable concentrates are the most common formulations used today. The solvent in many cases may tend to injure some crops and emulsifiable concentrates may require some slight agitation to maintain the suspension.

1.1.3.6 Microencapsulated

Microencapsulated pesticides are impregnated into tiny, slow release plastic beads and mixed into a liquid. This

formulation reduces dermal toxicity and increase residual efficacy.

1.1.3.7 Wetting Agents or Surfactants

These are used to improve spread of a spray mixture on foliage. Surfactants are most commonly used to apply pesticides on plants that have waxy or hairy leaves. Surfactants help to increase the uptake of chemicals.

1.1.3.8 Aerosols

Aerosols contain pesticide dissolved in a liquid and held up under pressure. A fine mist is expelled when this mixture is released by a pressure valve on the container. Aerosols are most appropriate for use within buildings, although there are types available for limited outdoor treatment. Insecticidal fogs generated by heating a mixture of an insecticide in a solvent such as kerosene utilize a similar principle. The fogs are used outdoors to control certain flying insects such as mosquitoes and flies. Aerosols sometimes cause drift problems.

1.1.3.9 Fumigants

Fumigants are volatile pesticides that kill pests with vapours. These can be used only where the gas can be confined, such as in storage bins, in the soil, within building or under gas-tight tarps. Fumigants are effective against nematodes, weeds, fungi and insects.

1.1.4 Degradation of Pesticides

Pesticide degradation, or the breakdown, is usually beneficial. During degradation, the pesticides change into inactive,

less toxic, and harmless compounds. However, degradation is detrimental when a pesticide is destroyed before the target pest has been controlled. Three general types of pesticides degradation are microbial, chemical and photo degradation.

Microbial degradation [9,10] is the breakdown of pesticide by fungi, bacteria, and other micro-organisms that use pesticide as a food source. Most microbial degradation of pesticide occurs in the soil. Soil conditions such as moisture, temperature, aeration, pH and the amount of organic matter affect the rate of microbial degradation because of their direct influence on microbial growth and activity. The frequency of pesticide applications can also influence microbial degradation. Rapid microbial degradation is more likely when the same pesticide is used repeatedly in a field. Repeated applications can actually stimulate the build up of organisms effective in degrading the chemical. As the population of these organisms increases, degradation accelerates and the amount of pesticide available to control the pest is reduced.

Chemical degradation is the breakdown of pesticide by processes that do not involve living organism. Besides the physical and chemical properties of the pesticides, temperature, moisture, pH and adsorption to soil determine the reaction that would take place.

One of the most common pesticide degradation reaction is hydrolysis.[11,12] In this breakdown process the pesticides react with water. Depending on the nature of pesticide, the hydrolysis may occur in acidic and/or alkaline conditions. Many organophosphate and carbamate insecticides are particularly

susceptible to hydrolysis under alkaline conditions. Some are actually broken down within a matter of hours when mixed with alkaline water.

Photo degradation[13,14] is the breakdown of pesticide by light, particularly the sunlight. Photo degradation can destroy pesticide on foliage, on the soil surface and even in the air. Factors that influence pesticide photo degradation include the intensity of the sunlight, properties of the application site, and the properties of the pesticide.

1.2 Surfactants, Classification, Properties and Application

Surfactants or surface-active agents[15] commonly known as soaps and detergents, are amphiphiles that contain both apolar, hydrophobic and polar hydrophilic groups. They concentrate at air- water interfaces and in water, or similarly strongly hydrogen-bonded solvents, they self associate at concentrations above the critical micelles concentration, cmc, to form association colloids, known as micelles.[16,17] In the lower range of concentrations of surfactant, micelles are typically spherical with alkyl groups in the interior and radii slightly larger than extended alkyl chain lengths. But, with increasing concentrations of surfactant, and on addition of hydrophobic solutes or low charge density ions, micelles grow and become ellipsoidal. Addition of co-surfactants and apolar solvents generates microemulsions, a more ordered structure form with more concentrated surfactant.[18] Association colloids have interfacial regions containing ionic or polar head groups and ionic and polar solutes may be incorporated in this region. Considerations of the dimensions of head groups and apolar tails indicates that the volume of the interfacial region is approximately half that of the total micelles. Solutions of dilute surfactants are isotropic containing submicroscopic particles, which form a micellar pseudophase distinct from the aqueous pseudophase. The interfacial region is highly anisotropic.

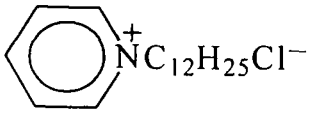
The unusual properties of aqueous surfactant solutions can be ascribed to the presence of a hydrophilic head group and a hydrophobic chain (or tail) in the molecule. The polar or ionic head group usually interacts strongly with an aqueous environment, in which case it is solvated via dipole-dipole or

ion-dipole interactions. On the basis of the nature of the polar head group, surfactants can be divided the following categories.

1.2.1 Cationic

The cation of the compound is the surface active species. The most prevalent cationic surfactants based upon quaternary nitrogen include alkylammonium halides and tetra-alkylammonium halide. Pyridine and related species such as quinoline, isoquinoline, pyrazine, and their derivatives form the basis for a wide class of aryl based quaternary surfactants. Although less numerous, phosphorus can also be quaternarized with alkyl groups to provide alkylphosphonium surfactants.

Examples

Cetyltrimethylammonium bromide	$CH_3(CH_2)_{15}\overset{+}{N}(CH_3)_3Br^-$
Dodecylamine hydrochloride	$CH_3(CH_2)_{11}\overset{+}{N}H_3\,Cl^-$
Dodecylpyridinium chloride	

1.2.2 Anionic

Alkali alkanoates (or soaps) are well known anionic surfactants. The ionization of carboxyl group provide the anionic charge. Sodium dodecylbenzene sulfonate (SDBS) has effectively replaced soaps. Alkyl sulfates, alkyl ether sulfates, alkyl sulfonates, secondary alkyl sulfonates, aryl sulfonates, methylester sulfonates, and sulfonates of alkylsuccinates are other important classes of anionic surfactants. The fatty acids and sulfo compounds include the three most important anionic groups: corboxylate ($-CO_2^-$), sulfate ($-OSO_3^-$), and sulfonate

($-SO_3^-$). On the basis of basicity and phase data their hydrophilicity ranking is given as:

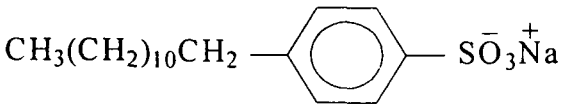
$$-CO_2^- >> -SO_3^- > -OSO_3^-$$

Examples

Potassium laurate $CH_3(CH_2)_{10}COO^- K^+$

Sodium dodecyl sulfate $CH_3(CH_2)_{11}OSO_3^- Na^+$

Sodium dodecylbenzene sulfonate



1.2.3 Nonionic

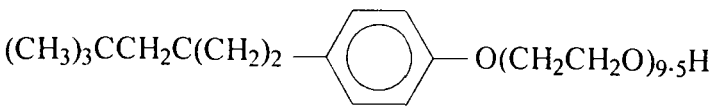
The water-soluble moiety of this type can contain hydroxyl groups or a polyoxyethylene chain. Many nonionic surfactants are structurally analogous to anionic and cationic surfactants, except that the headgroup is uncharged. Most prevalent among the headgroups of nonionics are oligomers of ethylene oxide. Simple saccharides such as glucose and sucrose are also common as headgroups for nonionic surfactant. The most widely studied class of alkyl ethylene oxide surfactant, also called alcohol ethoxylates, is represented as CxEy where x is the length of the alkyl chain and y is number of ethylene oxide unit in the head group. A related class is that of the alkyl phenol ethoxylates. Triton X-100 (TX-100) is perhaps the best known member of this class.

Examples

N, N-dimethyldodecylamine oxide $CH_3(CH_2)_{11}N(CH_3)_2 \rightarrow O$

Polyoxyethylene monohexadecyl ether $CH_3(CH_2)_{15}O(CH_2CH_2O)_{21}H$

Polyethylene glycol (t) – Octylphenyl ether, TX-100



1.2.4 Zwitterionic

This type of surfactants can behave as either cationic, anionic or nonionic species depending on the pH of solution. True zwitterions such as α-amino acids, can become ionized by intramolecular proton transfer.

$$NH_2CH(R)\,CO_2H \leftrightarrow N^+H_3\,CH\,(R)\,CO_2^-$$

Considerations of phase data and basicity[19] suggest that the relative hydrophilicities of ammonio zwitterionics decrease in the following order:

$$\text{ammonio} - CO_2^- \;>>\; \text{ammonio} - SO_3^- \;>\; \text{ammonio} - OSO_3^-$$

The betaines are very important class of zwitterionic surfacatants and include alkylbetaines, amidoalkylbetaines and heterocyclic betaines.

Examples

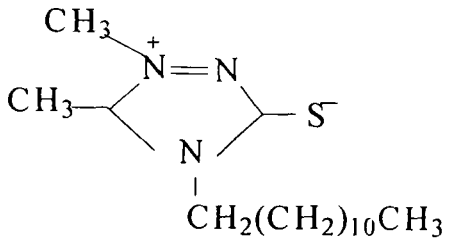
N – dodecyl – N : N-dimethyl betaine

$$C_{12}H_{25}N^+\,(CH_3)_2CH_2COO^-$$

3- (dimethyldodecylammonio) propane-1- sulfonate

$$CH_3\,(CH_2)_{11}\,N^+\,(CH_3)_2CH_2{-}CH_2{-}CH_2{-}SO^-_3$$

2, 3 dimethyl-3- dodecyl- 1.2,4- triazolium- 5 thiolate



1.2.5 Micelle Formation and Critical Micelle Concentration (CMC)

The formation of micelles in aqueous solution is generally viewed as a compromise between the tendency for alkyl chains to

avoid energetically unfavorable contacts with water, and the desire for the polar part to maintain contact with aqueous environment. A thermodynamic description of the process of micelle formation includes a description of both electrolyte and hydrophobic contribution to the overall Gibbs energy of the system. Hydrocarbon and water are not miscible, the limited solubility of hydrophobic species in water can be attributed to the hydrophobic effect. The transfer of the carbon solute from the hydrocarbon solvent to water is accompanied by an increase in the Gibbs transfer energy.[20] The decrease in entropy is thought to be the results of the breakdown of the normal hydrogen bonded structure of water accompanied by the formation of differently structured water, around the hydrocarbon chain. The presence of the hydrophobic species promotes an ordering of water molecules in the vicinity of the hydrocarbon chain. The overall process has the tendency to bring the hydrocarbon molecule together, which is known as hydrophobic interaction. Molecular interaction arising from the tendency for the water molecule to regain their normal tetrahedral structure, and the attractive dispersion force between hydrocarbon chains, act cooperatively to remove the hydrocarbon chain from the water leading to an association of hydrophobic chains.[18,21,22]

At a specific, higher surfactant concentration, known as the critical micelle concentration (cmc), molecular aggregates form micelles. The cmc is a property of the surfactant and a number of other factors including the temperature, pressure, and the presence and nature of additives. A low cmc is favored by increasing the molecular mass of the lipophilic part of the molecule, lowering the temperature and adding electrolyte. Surfactant molecular masses typically range from a few hundred up to several thousands.

The physico-chemical properties of surfactants vary markedly above and below the cmc value.[23-29] Below the cmc value, the physico-chemical properties (e.g., conductivities, electromotive force measurements) of ionic surfactants like sodium dodecyl sulfate, SDS resemble those of a strong electrolyte. Above the cmc value, these properties change dramatically, indicating a highly co-operative association process is taking place. The general way of obtaining the cmc value of a surfactant micelle is to plot an appropriate physico-chemical property versus the surfactant concentration and observe the break in the plot [30-32] (Figure 1.1).

Micelles are often considered as static structures of spherical aggregates of surfactant molecules. However, micelles are in dynamic equilibrium with surfactant monomers in the bulk, which are constantly being exchanged with the surfactant molecules in the micelles. The equilibrium between monomer and aggregate is established within a few milliseconds. At equilibrium the number of micelles formed in a given time is equal to the micelles disintegrated in the same time. Additionally, the micelles themselves are continuously disintegrating and reforming. The kinetics of micellization have been studied by various techniques such as stopped flow, temperature jump, pressure jump, ultrasonic absorption and spectrophotometry.[33-37] Polarity and water content in different regions of the micelles play an important role on the rate of reaction in these regions. The surface layer of micelle resembles concentrated electrolyte solution with a dielectric constant lower than that of the bulk water. The micellar phase is less polar than water and the ionic micelles have a polarity

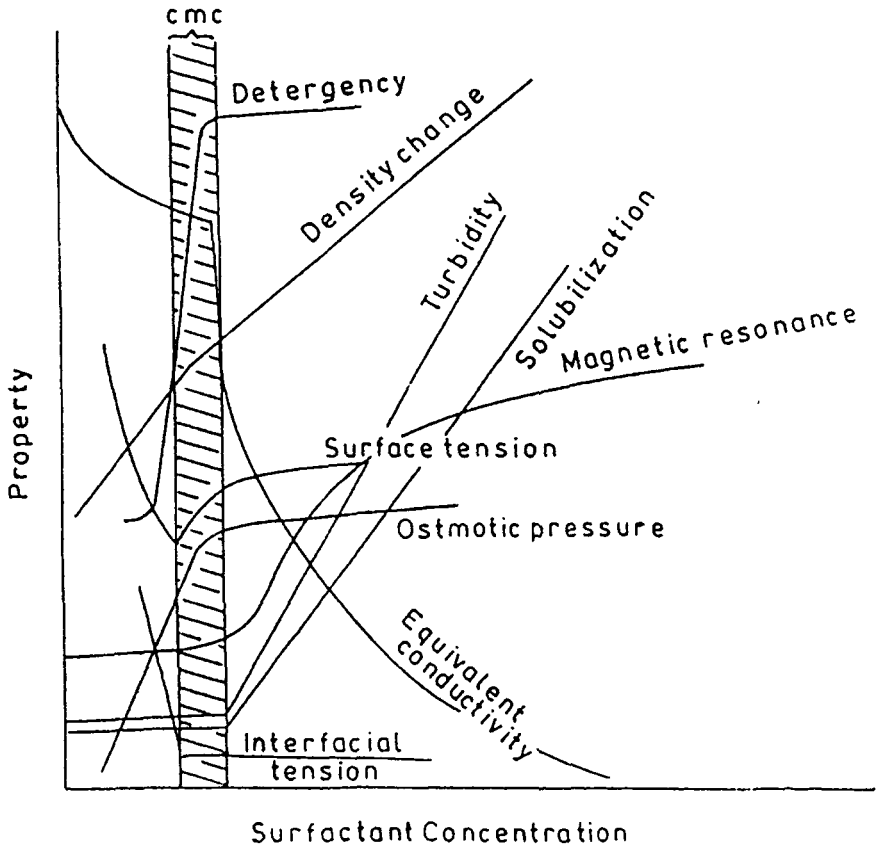


Figure 1.1 Variation of Physical properties with surfactant concentration

near to that of pure ethanol even at the Stern's layer.[38-40]

In case of ionic micelles, electrical charge on a micelle is nuetralized by counter ions in the electrical double layer around it as shown in Figure 1.2. The first layer immediately adjacent to its surface is called Stern's layer.[41] In this layer the counter ions are adsorbed so strongly that there is no thermal agitation and they migrate together with the colloids micelle in an electrical field. According to the most widely accepted model, head groups of surfactant molecules are situated in this layer. The remainder of the double layer is diffused and called Gouy-Chapman layer since the ions are diffused into the bulks solution as a consequence of the thermal motion. The decrease in counter ion concentration with the distance from the micellar surface has an exponential form.[42-45]

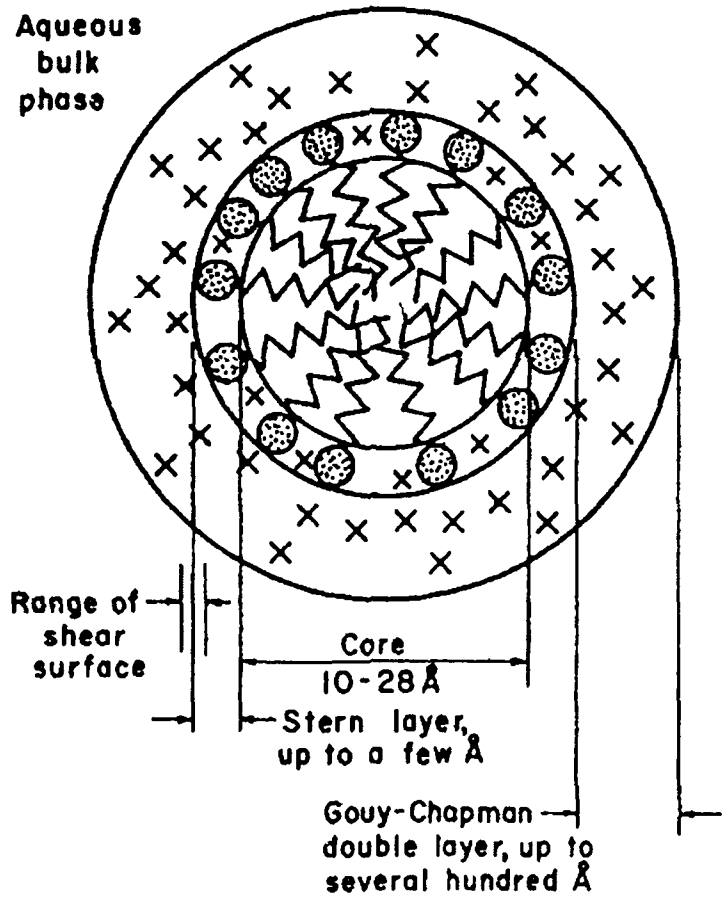


Figure 1.2: Model of a typical ionic micelles showing the location of the counter ions (×), the head group (⊙) and the hydrocarbon chain (^^^) .

1.2.6 Application of Surfactants

The cmc values are important in virtually all of the process industry surfactant applications, from mineral processing to formulation of personal care products[46] and foods,[47] to drug delivery systems,[48] and to new surfactant remediation technologies. In these processes, surfactant must usually be present at a concentration higher than the cmc. The greatest effect of the surfactant, whether in interfacial tension lowering, emulsification, suspension stabilization, as a delivery vehicle, or in promoting foam stability, is achieved when a significant concentration of micelles is present.

Surfactants are widely used in crop protection products [49,50] i.e., pesticides, herbicides, fungicides and insecticides.[51,52] The formulation of pesticides is significant in terms of product stability and product performance. The current trend in crop protection is towards products that are more potent, safer to user, having less impact on the environment, more convenient to use and improved efficiency of the applied products. In the case of sprayed products, colloid and interface science impacts all aspects of application. Spray droplets impact the leaf surface, creating a foliar deposit from which the pesticide moves into the leaf or contacts the pest.

In pesticide formulations, the inert ingredients usually are added to improve the effectiveness of the active ingredient. Surfactants are the inert ingredient and increase the efficiency of main ingredient. These inert ingredients usually determine the method of application. The most important formulations are dusts, sprays, wettable powders, flowables, emulsifiable concentrates, granules, baits and encapsulated pesticides. Surfactants are used in pesticide formulations as wetting

dispersing, emulsifying, solubilizing and bio enhancement agent. Wetting is a primary function of surfactant in pesticide formulations. It is incorporated into the formulation to facilitate satisfactory surface coverage of the agent. It is also used to increase the uptake of chemicals. The other important application of surfactant in pesticides formulations[53] are to increase the solubility of the pesticide in aqueous medium, to stabilize the pesticide by controlling evaporation or decomposition (above cmc), to enhance the effectiveness of the pesticide by providing the fine spray (below cmc). Surfactant are also used as emulsifying agent and allow insoluble pesticides to be applied in water.

Surfactants are involved in the production of many common food items[54,55] and can be found in the extraction of cholesterol, solubilization of oils, liquor emulsification, prevention of component separation, and solubilization of essential nutrients.

Cosmetic formulations are dependent on new formulation techniques[56,57] for emulsion, particularly for storage properties. Emulsion and microemulsion are characterized by fine droplet size which are highly stable. Microemulsion are useful for creating a clear formulation of O/W. Good cosmetic formulations also yield good skin-product interactions and therefore good penetration of active ingredient into the skin layers.

An emulsion is used in petroleum industry after primary and secondary cycles of oil recovery.[58-63] Chemicals may be injected to drive out additional oil in an enhanced oil recovery process, which may involve creating in situ emulsion in the reservoir. In the petroleum industry surfactant used as wettability alteration, enhanced micro

displacement of oil, stabilizing foams for mobility control or foam drilling fluids, separation and flotation aids in oil sands processing, heavy oil transportation as aqueous emulsion, enhanced aquifer remediation and breaking of oil emulsions.

Micelles exert large rate effects upon organic reactions and can in principle discriminate between different reactions, depending upon their charge type or molecularity. Bimolecular E_2 reactions involving OH^- in aqueous solution are speeded by cationic and inhibited by anionic micelles[64] whereas spontaneous S_N reactions are generally inhibited strongly by cationic micelles and less strongly by anionic micelles, it is therefore relatively easy to observe micellar control of product formation.

An ionic surfactant or phase-transfer catalyst can also be immobilized by binding it to an insoluble resin. The use of micelles in chemical analysis are rapidly increasing.[65] Analytical reactions are carried out typically on a small scale and are based on spectrophotometry.

1.3 Kinetic Treatment of Reactivities in Micellar System

Ionic colloidal assemblies e.g., micelles, microemulsions, hemimicelles (solids), bilayers and vesicles are believed to be mimetic agent for membranes in biological system.[18] It has also been observed that there are structural similarities between globular proteins and spherical micelles and analogies between the catalytic effects of enzymes and functional micelles between catalysis and phase transfer catalysis. For these reasons numerous investigators[66-70] have focussed their attention on micelles and reactions in micellar media.

A number of important thermodynamic and kinetic studies of organic reactions specially with pesticides and herbicides have been performed in micellar solutions.[71-77] Aqueous micelles and other associated colloids have been observed to influence reaction rates and equilibria and concentration, or depletion of reactants in the interfacial region.[23,78-82] The interfacial region differs from water as a reaction medium,[83-86] which can affect rates of spontaneous reactions. These effects depend upon the transfer of substrate from water to micelles, the reaction mechanism and properties of the interfacial region, i.e., local charge, polarity and water content. Usually, spontaneous reactions that are accelerated by decrease in solvent polarity e.g., anionic decarboxylation and dephosphorylation, are accelerated by micelles and most spontaneous hydrolysis that are accelerated by increase in solvent polarity are inhibited in the presence of surfactants. The major problem in modelling chemical reactivity in many surfactant systems has been to describe the effect of surfactant and counter ion concentration and counter ion type on

the distribution of ionic reactants. Several models have been developed in which most of the kinetic results in micellar media have been interpreted satisfactorily with the help of Poisson-Boltzman Equation (PBE)[87-90] model and Pseudophase Ion Exchange (PIE)[91-94] model.

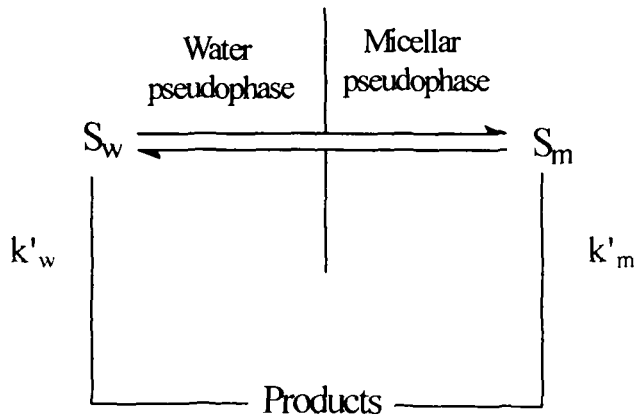
1.3.1 Poisson-Boltzman Equation Model (PBE)

In this model, the electrostatic interactions are assumed to attract counter ions to the micellar surface but repel co-ions, and ion distributions are estimated by solving the Poisson-Boltzman equation in the appropriate symmetry. A simple formalism that has been applied kinetically involves the assumption in which micelles are spherical and monodisperse. If ions are treated as point charges, which interact only coulombically with the micelle, ion specificity is lost, and a term was therefore added for non-coulombic interactions which should be small for hydrophilic, high charge density ions and larger for polarizable ions.[95,96] These specifically interacting ions should neutralize ionic head groups and reduce the micellar charge density. Therefore, interionic competition is introduced, but without the one to one exchange of the simple PIE model. This treatment fits kinetic data for ions e.g., Cl^- or Br^-, which are reactive, as in S_{N2} reactions, or are inhibiting reactions of other ions.[97] It also fits ionic distributions, based on NMR spectrometry, and explains why Cl^- and Br^- displace ions such as OH^-, whereas very hydrophilic ions such as OH^- or SO_4^{2-} are ineffective in displacing Cl^- and Br^-, even when they are in very large excess.

The treatment involves disposable parameters e.g., the term for ion specific interactions and the size of the reaction region at the micellar surface. The assumption of a "smooth" micelle[98] and neglect of finite ion correlation and size[99] are oversimplification in this model and one expects it to fail if micelles become highly polydisperse. The PBE treatment predicts that the counter ions and co-ions are respectively in negative and positive concentration gradients extending radially from the surface. An increase in ionic concentration markedly reduce both positive and negative concentration gradients.

1.3.2 Pseudophase Ion Exchange Model (PIE)

In this pseudophase ion exchange model, the totality of the micelles in solution is treated as a separate pseudophase uniformly distributed in the aqueous phase. Above cmc, a micellar-catalyzed bimolecular reaction is described in terms of the distributions of reactants between the micellar and aqueous pseudophases. The reaction occurs in both aqueous and micellar pseudophases according to the following scheme 1.1.



Scheme 1.1

In this scheme k'_w and k'_m are first order rate constant, and (D_n) is total [surfactant] less [monomer] which is assumed to be the cmc, under kinetic conditions.[23,68] Corresponding to the scheme 1.1, the overall first order rate constant is given by:

$$k_\psi = \frac{k'_w + k'_m K_s [D_n]}{1 + K_s [D_n]} \qquad (1.1)$$

where K_S is an association constant in terms of micellized surfactant. The subscript *w* and *m* denotes aqueous and micellar pseudophases, respectively and quantities in squared bracket are concentrations in terms of total solution volume. The values of k_ψ increases or decreases with $[D_n]$ to a constant value of $k_{obs} = k'_m$, when substrate is fully micellar bound. The treatment also fits inhibition of bimolecular reactions with dilute hydrophilic, co-ions which remain in water while micelles incorporate hydrophobic substrate.[18,24,67] Kinetic values of K_s generally agree with those estimated or measured directly. The values of k'_m / k'_w are consistent with this difference in polarity, based on kinetic solvent effect.[78]

This treatment fits a great deal of data for the kinetics of simple, spontaneous, unimolecular or water catalyzed reactions. The treatment also fits for the inhibition of bimolecular reactions with dilute, hydrophilic, co-ions, which remain in water while micelles incorporate hydrophobic substrates. The equation (1.1) could be rearranged in the form similar to Lineweaver- Burk equation (1.2).

$$\frac{1}{k_\psi - k'_w} = \frac{1}{k'_m - k'_w} + \frac{1}{(k'_m - k'_w) K_s ([D_n] - \text{cmc})} \qquad (1.2)$$

The equation (1.2) permits calculation of k'_m and K_s, provided that k'_w is known[68]. These equations (1.1 and 1.2) have been used extensively and provided the basis for quantitative analysis of micellar rate effects.

The equations (1.1 and 1.2) generally fail to explain the micelles catalyzed bimolecular reactions. According to equation (1.1) the first-order rate coefficient should reach a constant, limiting value at high surfactant concentration when the substrate is fully micellar bound. But in most of the non-solvolytic bimolecular reactions the rate- [surfactant] profile shows a rate maxima behavior. The influence of the surfactant concentrations on rate can be treated quantitatively by taking into account the distribution of both reactants between water and micelles. This is done by expressing the first order rate constant k'_w and k'_m in terms of the second-order rate constants in water and micelles, and reactant concentrations in each pseudophase.[25,100-103] The concentration of reactant in micellar pseudophase can be given in terms of mole ratio. However, this approach does not allow direct comparison of second order rate constants in aqueous and micellar pseudophases. The first order rate constants are written in equations (1.3) and (1.4) in terms of second order rate constants, k_w and k_m for reaction of a reagent Y.

$$k'_w = k_w [Y_w] \qquad (1.3)$$

$$k'_m = k_m m_Y^S \qquad (1.4)$$

where the mole ratio, $m_Y^S = [Y_m]/([D_n] - cmc)$.

By combining the equations (1.1) (1.3) and (1.4), expressions (1.5) and (1.6) are obtained.

$$k_{\psi} = \frac{k_w[Y_w] + k_m K_s m_Y^S ([D_n] - cmc)}{1 + K_s ([D_n] - cmc)} \qquad (1.5)$$

$$= \frac{k_w[Y_w] + k_m K_s [Y_m]}{1 + K_s ([D_n] - cmc)} \qquad (1.6)$$

Addition of surfactant leads to binding of both reactants to micelles, and usually increases the reaction rate. Eventually, however, increase in surfactant concentration dilutes the reactants in the micellar pseudophase and the rate falls. This behavior supports the original assumption that substrate in one micelle does not react with reactant in another, and that equilibrium is maintained between aqueous and micellar pseudophases. In addition, widely observed inhibition by inert electrolytes is ascribed to competition between reactive and inert counter ions. The ionic concentration in the interfacial surface region is given by

$$N_M = (1 - \alpha)/ V_m \qquad (1.7)$$

Where α is the micellar fractional ionization.[79,104] Based on α-value in the range 0.2-0.4 and V_m = 0.2 M^{-1}, ionic concentration at the surface can be much higher than that in dilute aqueous electrolyte. Romsted extended this relation to mixed ion system by assuming that counter ions Y and M, compete as at ion- exchange resin.[25,27]

$$Y_m + N_w \rightleftharpoons^{K_N^Y} Y_w + N_m$$

The equilibrium constant for the concentration, Y and M between the micellar and aqueous psedophases are given by

$$K_N^Y = \frac{[N_m][Y_w]}{[N_w][Y_m]} \qquad (1.8)$$

Provided that α is constant, the mass-balance relation allow k_ψ to be related to concentrations of surfactant and reactive and inert electrolyte in terms of K_N^Y, α, rate constants. Values of K_N^Y, follow the Hofmeister series and agree with non kinetic evidence on ionic competition.[105] Low charge density ions displace high-charge density hydrophilic ions and the approximate anion affinity sequence is [78,79]

$$NO_3^- \approx Br^- \approx N_3^- > Cl^- > AcO^- > F^- \approx OH^-$$

The PIE model fits variations of k_ψ with concentrations of surfactant, reactive and inert ions and predicts the dependence of k_ψ on substrate hydrophobicity. PIE treatment fails when reactive ion is very hydrophilic, e.g., OH^- or F^- and is in high concentration.[106,107]

The PIE treatment does not predict satisfactorily the behavior of k_ψ - [surfactant] profile in case of very hydrophilic reactive ions e.g., OH^-, F^- and in high concentrations. The situation is different for reactions in functional micelles e.g., CTAOH or CTAF. With fully bound substrate, k_ψ increases sharply with increasing total concentrations of OH^- or F^- [106-108]. Several treatments have been proposed that retain ion-exchange model, but without the concept of a constant value of α which controls counter ion concentration at the micelle-water interface.

Bunton[106] assumed that the ionic- binding follows a Langmuir isotherm to explain the variation of k_ψ with [CTAOH] and added [OH^-]. The ionic equilibria for X^- in CTAX is given by

$$K'_X = \frac{[X_m^-]}{[X_w^-]([D_n]-[X_m^-])} \qquad (1.9)$$

If K'_X is large the concentration of X^- in the micelle is approximately independent of $[X_T]$, i.e., α is approximately constant, but if K'_X is small, this concentration increases with the total concentration. This so-called mass action treatment fit kinetic data and can be extended to system in which ions compete.[109-111]

Hall[112] discussed failure of the PIE treatment in terms of transition state theory and thermodynamics of interactions between solutes and association colloids, in particular between ions and ionic micelles. This treatment analyzes overall reaction rates by treating the activated complex as being in equilibrium with reactants, follows the Eyring rates equation. The activated complex in the bulk aqueous medium should therefore be in equilibrium with that in the micelles, although its lifetime is very short in terms of rates of solute transfer between water and micelles. Solutes enter micelles with diffusion-controlled rates.[112] Whereas the lifetime of the activated complex is that of a stretching vibration. Attack of a small nucleophilic anion, upon a nonionic substrate generates a larger anion, and reaction rates depend upon interactions of these species with their environment. Depending upon reaction mechanism there may be compensation between interactions of the initial and transition states. In this

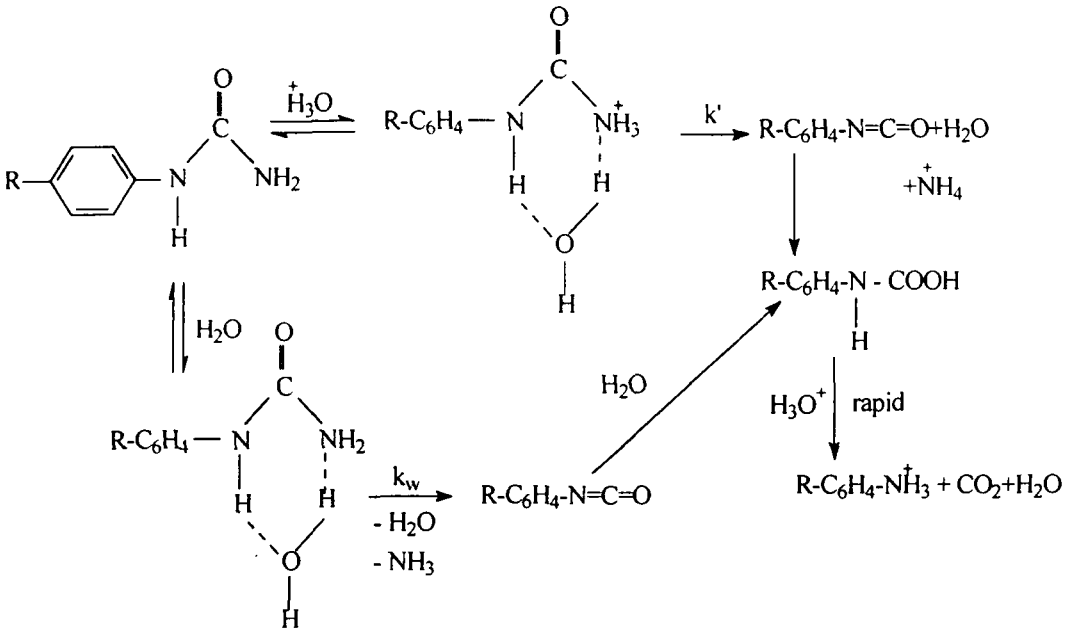
situation k_2^m and k_w should be similar in many bimolecular reactions, as indicated by the pseudophase treatment.

An important point in the transition state model is the demonstration that when the only counter ion is the reactive ion the form of the rate-surfactant profile depends upon the fractional micellar ionization, α.[112] If α is small as with CTABr, k_{obs}, with fully bound substrate, will not increase significantly with increasing [counter ion], but if α is larger, as with CTAOH, k_{obs} should increase markedly with increasing [counter ion], as is found.

1.4 Hydrolysis of Phenylureas

O'Connor and Barnett[113] reported the acidic hydrolysis of 3-methylphenylurea and 4-fluorophenylurea. They determined the rate constants for the hydrolysis of 3-methylphenylurea in the acid range range 2.5-60% and for 4-fluorophenylurea in the acidic concentration of and 2.5-70% w/w H_2SO_4 at five-temperatures in the range 70-110.4°C. On the basis of two term equation and high activation parameters they suggested that these phenylureas hydrolyze by A-1 mechanism.

The detailed mechanism of the hydrolysis of phenylureas namely 4-methyl-, 4-methoxy-, 4-ethoxy-, 4-isopropyl-, 4-n-butyl-, 4-chloro-, 4-Bromo-, 4-nitro-, and 3-nitro-phenylurea in acidic and aqueous solution were studied by Giffney and O'Connor[114]. They observed that the phenylureas were hydrolyzed in water without the formation of corresponding aniline. A decrease in the absorbance of the carbonyl peak was observed as the reaction progressed. But this absorbance did not tend to zero but shifted towards a new value of λ_{max}. On addition of a few drops of acid, the carbonyl peak collapsed immediately to give the spectrum of the corresponding aniline. Thus in the absence of acid, there is a build-up of a product which has been identified as the corresponding carbamic acid. In acidic solution carbamic acids are very unstable and decompose readily to form aniline and carbon dioxide. The following mechanism was proposed (Scheme 1.2).

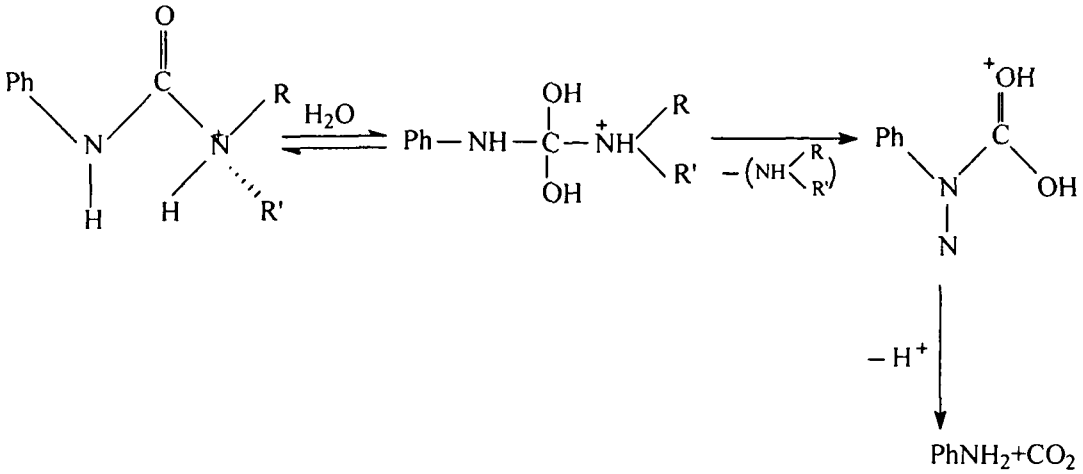


Scheme 1.2

The kinetics of hydrolysis of phenylurea herbicides namely fenuron, monuron, diuron and chloroxuron were studies by Sabaliunas *et al.*[115] at temperatures 64°C and 84°C in alkaline and neutral media. They suggested the mechanism in which hydroxide ion promoted reactive tetrahedral intermediate anion is formed. This intermediate can either revert to the starting compound, decompose to products, or react with a second hydroxide to form a dianion, prior decomposition to products.

Laudien and Mitzner[116,117] investigated the kinetics and mechanism of the hydrolytic decomposition of phenylureas in acidic and basic media. In acidic medium, authors studied the hydrolysis of phenylureas, kinetically in acidic water-methanol solutions (9:1) at 80°C and 90°C. They reported that the rate of hydrolysis of phenylureas is not directly proportional to the hydronium ion concentration, but rises with the acid strength only in solution of low acidity, whereas it passes through a

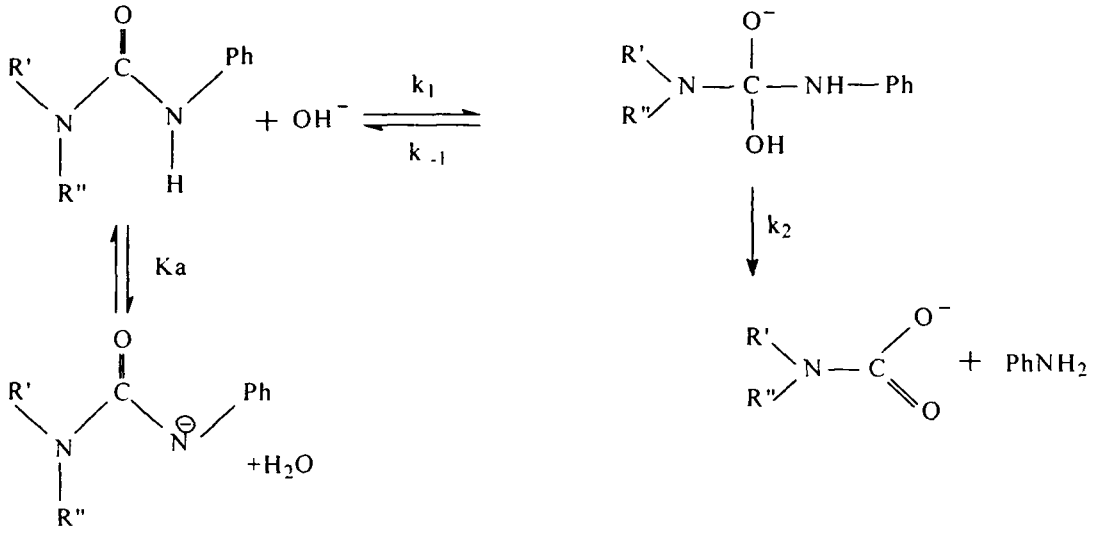
maximum and decrease again in stronger acidic solution. They proposed the mechanism for the acidic hydrolysis of phenylureas presented in scheme 1.3. In the course of hydrolytic decomposition, the substrate is first protonated followed by rate determining attack by water. The tetrahedral intermediate then decomposes to an amine and a phenyl carbamic acid which again decarboxylates very quickly under acidic conditions to form the corresponding aniline.



Scheme 1.3

The basic hydrolysis of phenylureas were studied in the pH range 12-14 in water- methanol (9:1) solution at 80°C and 90°C. The authors[117] observed that the rate of hydrolysis of phenylureas is not directly proportional to the hydroxide ion concentration, but tends towards a limiting value at high hydroxide ion concentration. They found that in weakly basic media the hydrolysis of phenylurea presumably occurs via an addition-elimination mechanism in which an intermediate hydroxide ion addition complex is formed. Water acts as a general acid protonates the leaving group to facilitate its elimination. In stronger alkaline media, the formation of conjugate base of

phenylurea caused by a deprotonation of the aryl-NH group through ion gains in significance. This conjugate base is inactive towards hydrolysis, as the resonance in the anion, increases the double bond character of the C-N bond compared to that in the urea and thereby stabilizes it against cleavage. Besides, the increased electron density impedes the attack of the hydroxide ion at the carbonyl carbon to form the intermediate tetrahedral complex.



Scheme 1.4

Salvestrini *et al.*[118] carried out the detailed kinetics and mechanistic studies of hydrolysis of phenylureas namely diuron, isoproturon, neburon and chlorotoluron. The rate of hydrolysis was found to be affected by temperature, pH and buffer concentration. An intermediate phenyl isocyanate is formed via another intermediate zwitterion. The formation of zwitterion depends on pH and buffer concentrations and are produced through three parallel routes .At low pH, specific acid-general base catalysis, followed by slow deprotonation of a nitrogen atom by a general base was observed. At high pH, specific basic

general acid catalysis, followed by slow protonation of a N-atom by a general acid and at intermediate pH the reaction proceeds through a proton switch promoted by buffers. Bifunctional acid-base buffers such as HCO_3^- / CO_3^{2-}, $H_2PO_4^-$ / HPO_4^{2-} and CH_3COOH/CH_3COO^- are very efficient catalysts. At high buffer concentration, as well as pH < 3 or > 12, the breakdown of the zwitterion was rate determining step

The poor solubility and the use of micellar media in pesticides and herbicide formulation prompted many workers to study the effects of surfactants on the kinetics of hydrolysis of pesticides. Mollet and O'Connor[119] reported the effects of micelles on the solubilization and decomposition of 4-methyl and 4-nitrophenylurea. The value of cmc of non-ionic nonyl phenoxypoly (oxyethylene)-14 ethanol (A-730) and cationic hexa decyltrimethylammonium bromide (CTAB) were increased on addition of very small amounts of 4-methyl-and 4-nitrophenylureas. The micelles of A-730, CTAB and anionic sodium dodecyl sulfate (SDS) have little effect on the rate constants of hydrolysis of these phenylureas.

Matondo *et al.*[120] carried out a detailed investigation for the influence of SDS and CTAB on the kinetics of hydrolysis of phenyl, methyl and dodecyl N-(4-pyridyl) carbamates in H_2O-dioxane solutions. The SDS micelles reduced the rate of hydrolysis of phenyl and methyl N-(4-pyridyl) carbamate while the CTAB micelles speeded up the hydrolysis rate of phenyl carbamates and decreased the rate constant for methyl carbamate. They explained their results in the presence of surfactants on the basis of pseudophase model. Inhibition of the rate of hydrolysis

of dodecyl (4-pyridyl) carbamate by SDS and CTAB were attributed to the tensioactive character of these substances.

The kinetics of alkaline hydrolysis of the dicarboximide fungicides namely procymidone, iprodione, vinclozolin, and chlozolinate were investigated in the micellar media by Villedieu *et al.*[121] They studied in solution containing various amounts of either sodium dodecyl sulfate (SDS), cetyltrimethylammonium bromide (CTAB), or three non ionic surfactants (two C_{13} alcohols and a copra amine combined with ethoxy chains) and compared with the kinetics in aqueous media. For all compounds, the rate constants observed were slightly reduced by the SDS micellar media, showing that reactions essentially took place in the aqueous pseudophase. The CTAB micellar media speeded up the hydrolysis rates with small quantities of Br^- ions in the medium. As the number of Br^- ions increases, the rate of reactions fall. This is characteristics of an ion exchange (OH^- and Br^-) at the surface of the CTAB micelles. The presence of non- ionic micelles had little influence on the rate of hydrolysis of the fungicides. The inhibition in the rate of dicarboximide ring opening is attributed to micelle-substrate association. The results were explained by means of the pseudophase kinetic model coupled with the mechanism of hydrolysis of these fungicides in water.

The kinetics of cleavage of paraxon and parathion pesticides by cetyltrimethylammonium iodosobenzoate were investigated by Moss *et al.*[122] They observed that cetyltrimethylammonium iodosobenzoate (CTA)IBA is highly reactive towards paraxon and parathion. In aqueous solution at pH 9.0 excess (CTA)IBA mediates their hydrolysis with

$k_{obs\ (max)}$ = 0.014 and 0.0030 s^{-1} respectively. Parathion is more hydrophobic than paraxon and consequently bind more strongly to CTA micelles. This results into the sharp rise of k_{obs} with increasing surfactant concentration for parathion than paraxon. Another consequence of the stronger binding of parathion is that k_{ψ} (max) is obtained at a lower surfactant concentration for parathion relative to paraxon.

Bakeeva *et al.*[123] reported the kinetics of reactivity of alkaline hydrolysis of thiophosphate in micellar and hexagonal phase of cetyldimethylethylammonium bromide / NaOH / water system. Reactivities of o-p-nitrophenyl-o-o-dimethyl thiophosphate, o-p-nitrophenyl-o-o-diethyl thiophosphate and o-p-nitrophenyl-o-o-dimethylphosphate in the cetyldimethylethylammonium bromide (CDAB)/ NaOH/ water system and hexagonal (E) phase were investigated with the help of spectrophotometric method. Binding constants and rate constants in micellar pseudophase were obtained from kinetic dependence of k_{obs} on [CDAB] in accordance with the pseudophase model. The micelles accelerated the alkaline hydrolysis of o-p-nitrophenyl-o-o-dimethyl thiophosphate and o-p-nitrophenyl-o-o- diethylphosphate by 6 and 8 times.

1.5 Statement of the Problem

The phenylureas are the active principle of herbicides widely used in agriculture.[4,5] Presently about 25 phenylureas are marketed and are used as pre or post emergence herbicides for the control of annual grasses and broad leaved weeds in cereals. The solubility of these compounds in water is low in the order of ~ 10^{-4} mol L^{-1}. When they are spread in the environment, only a small proportion of it reaches targets. Surfactants are commonly used in the pesticide formulations to improve the effectiveness of the active ingredient. Surfactants are also used to solubilize and to improve the spread of a spray mixture. Micelles are considered as model for enzyme action because they are similar in shape and size, and more importantly, both have hydrophobic core and polar surfaces. Micelles affect the rate of reaction due to several factors; by differential distribution of the substrates inside and outside the micelles and by perturbing the thermodynamic parameters of the reaction. The concentration of reactants into a small volume through electrostatic and / or hydrophobic interactions is the main factor involved in the kinetic micellar effects on bimolecular reactions.

Keeping in view of the importance of phenylureas as herbicides and surfactants as solubilizing and spraying media, the present work on the hydrolysis of isoproturon and fenuron in surfactant media has been undertaken. The work includes the detailed kinetics and mechanism of hydrolysis of isoproturon and fenuron in acidic and alkaline media. The influence of micelles on the rate of hydrolysis has also been studied and discussed. The

study will be helpful to understand and predict the fate of these compounds after their dispersal in the environment. The stability of these ingredients in the formulations of surfactants can also be predicted.

The work described in this thesis comprises the following three chapters.

Chapter 2 : Experimental

Chapter 3 : Kinetics of the acidic hydrolysis of isoproturon and fenuron in CTAB and NaLS micelles.

Chapter 4 : Kinetics of the alkaline hydrolysis of isoproturon and fenuron in CTAB and NaLS micelles.

Chapter-2

Experimental

2.1 Materials

The chemicals used throughout the experimental work are listed in Table 2.1. The surfactants (CTAB and NaLS) were used as received. However their purities were ascertained by the absence of minima in surface tension versus log [surfactant] plots. Rest of the chemicals mentioned in Table 2.1 were used without further purification.

2.2 Preparation of Solutions

Water used to prepare the solutions was doubly- distilled over alkaline $KMnO_4$ in an all-glass (pyrex) distillation set-up. The specific conductivity of this water was in the range (1-2) × $10^{-6}\Omega^{-1}$ cm^{-1}

2.2.1 Pesticide Solutions

Stock solutions of phenylureas (Isoproturon and Fenuron) were prepared in methanol.

2.2.2 Surfactant Solutions

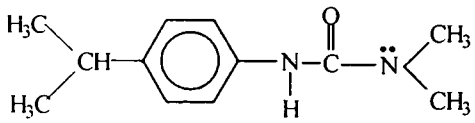
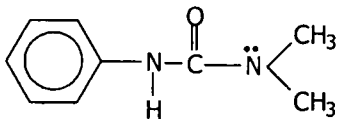
Surfactant solutions were prepared by dissolving appropriate amount of CTAB and NaLS in the doubly distilled water.

2.2.3 Other Solutions

Stock solutions of hydrochloric acid, sulfuric acid, sodium hydroxide, potassium nitrate, potassium chloride, and sodium chloride were prepared in distilled water.

Table 2.1

Name and Structural Formulas of the Chemicals Used

Name	Abbreviation	Structure/ Formula	Make	% Purity
Pesticides				
Isoproturon			Siris Crop Sciences Limited, New Delhi, India	95
Fenuron			Bharat Pesticides Company Limited, Bombay, India	98
Surfactants				
Cetyltrimethylammonium bromide	CTAB	$CH_3(CH_2)_{15}N^+(CH_3)_3Br^-$	CDH, India	99
Sodium lauryl sulfate	NaLS	$CH_3(CH_2)_{11}OSO_3^-Na^+$	CDH, India	99
Solvent				
Methanol	MeOH	CH_3OH	Qualigens, India	99

Name	Abbreviation	Structure/ Formula	Make	% Purity
Salts				
Sodium chloride	-	NaCl	Pfizer, India	99.9
Potassium chloride	-	KCl	CDH, India	99
Potassium nitrate	-	KNO_3	CDH, India	99
Acids				
Hydrochloric acid	-	HCl	Qualigens, India	35
Sulfuric acid	-	H_2SO_4	Merck, India	98
Base				
Sodium hydroxide	-	NaOH	Merck, India	97

2.3 Kinetic Measurements

The requisite amounts of surfactant, sodium hydroxide/ hydrochloric acid and methanolic solution of phenylurea were taken in a three-necked reaction vessel which was fitted with a double surface condenser to check any evaporation. The reaction vessel was kept in a thermostated water bath at the desired temperature (±0.1 °C). The progress of reaction was monitored by measuring the absorbance at constant intervals of time on Elico SL-164 UV-VIS spectrophotometer using 1 cm path length quartz cuvettes. The reaction was followed upto the completion of ~75% (i.e., 2 halves life-periods) of the reaction. All the kinetic experiments were run under the first order reaction condition in which the concentration of OH^- / H^+ and surfactant were kept in large excess (×10) over isoproturon / fenuron concentration.

During alkaline hydrolysis of phenylureas the corresponding carbamate is formed with slightly different value of λ_{max}. On addition of few drop of sulfuric acid, the carbonyl peak collapse immediately to give the spectrum of corresponding aniline (Figures 2.1-2.2). The absorption spectra were remain unchanged in the presence of surfactant. The absorbance for the extinction of isoproturon was measured at 240 nm and for fenuron at 239 nm. The acidic hydrolysis of phenylureas yields aniline and carbon dioxide and the spectra are given in Figures 2.3-2.4. The pseudo-first order rate constants were determined from the slope of *l*n $(A-A_\alpha)$ versus time, where 'A' is the absorbance of phenylurea at various intervals of time. The value

of A_α was obtained after refluxing the reaction mixture containing the requisite amount of phenylurea, and NaOH / HCl for 2 hours.

The cmc values of NaLS and CTAB containing phenylurea and sodium hydroxide / hydrochloric acid were determined conductometrically and are given in Table 2.2.

Table 2.2 CMC Values of Surfactants in Presence of Phenylureas

Pesticides	Surfactants	Acid/ Base	Temperature	CMC
Isoproturon +	CTAB +	HCl	at 70 °C	8.02×10^{-4}
Isoproturon +	CTAB +	NaOH	at 70 °C	8.04×10^{-4}
Isoproturon +	NaLS +	HCl	at 70 °C	8.36×10^{-3}
Isoproturon +	NaLS +	NaOH	at 70 °C	8.32×10^{-3}
Fenuron +	CTAB +	HCl	at 80 °C	8.52×10^{-4}
Fenuron +	CTAB +	NaOH	at 80 °C	8.26×10^{-4}
Fenuron +	NaLS +	HCl	at 80 °C	8.64×10^{-3}
Fenuron +	NaLS +	NaOH	at 80 °C	8.61×10^{-3}

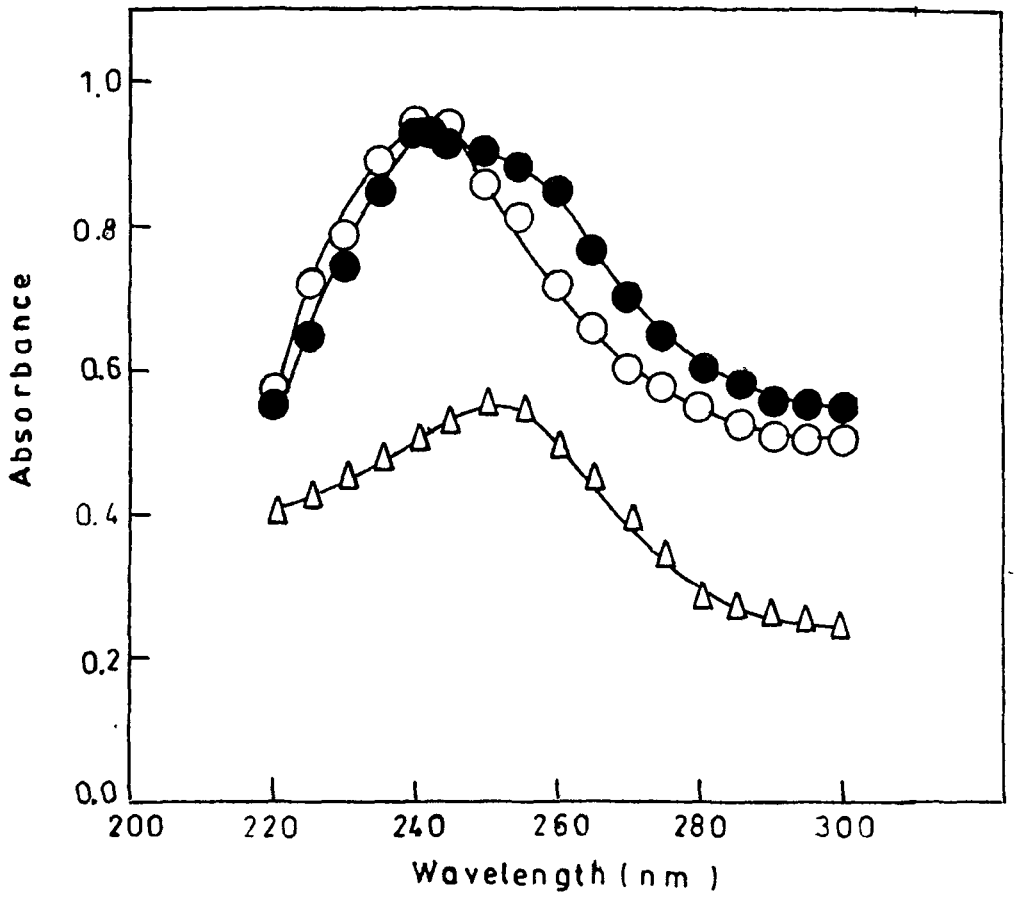


Figure 2.1 Absorption spectra of isoproturon (5.0×10^{-5} mol dm^{-3} in 0.1 mol dm^{-3} NaOH), (○) before refluxing, (●) after refluxing for 2 hours, and (Δ) after refluxing and adding H_2SO_4.

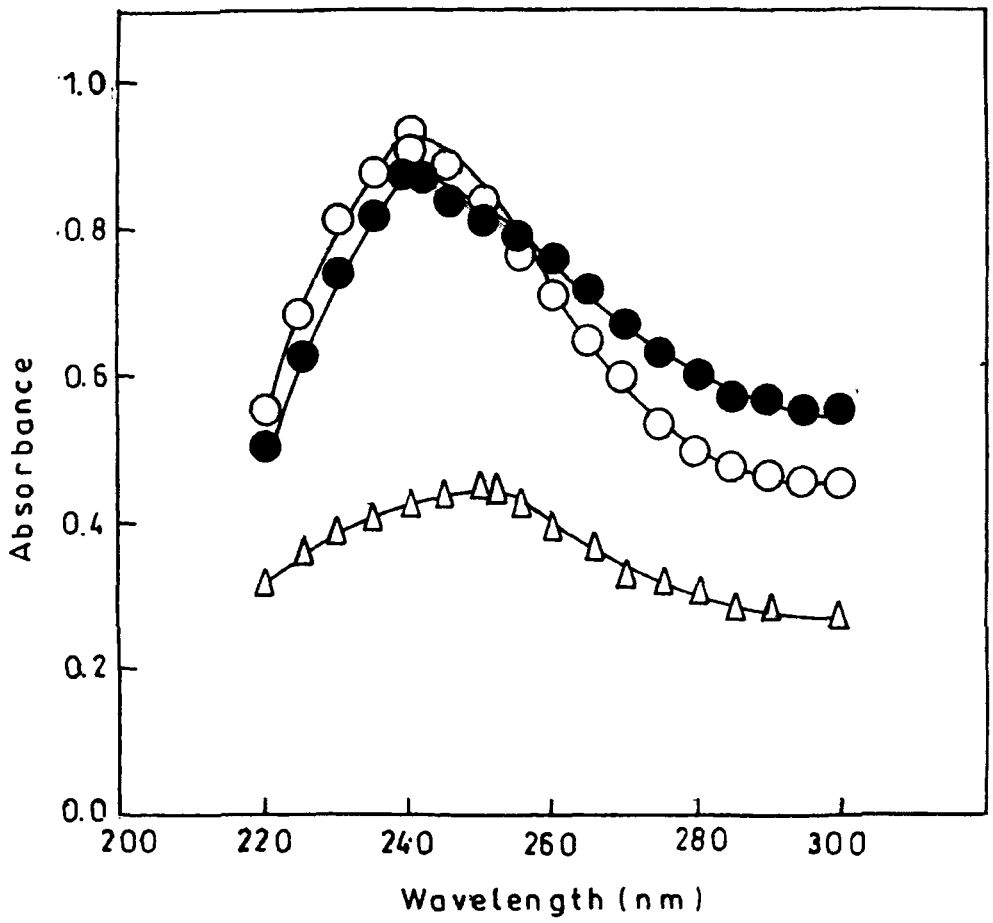


Figure 2.2 Absorption spectra of fenuron (5.0×10^{-5} mol dm^{-3} in 0.1 mol dm^{-3} NaOH), (○) before refluxing, (●) after refluxing for 2 hours, and (Δ) after refluxing and adding H_2SO_4.

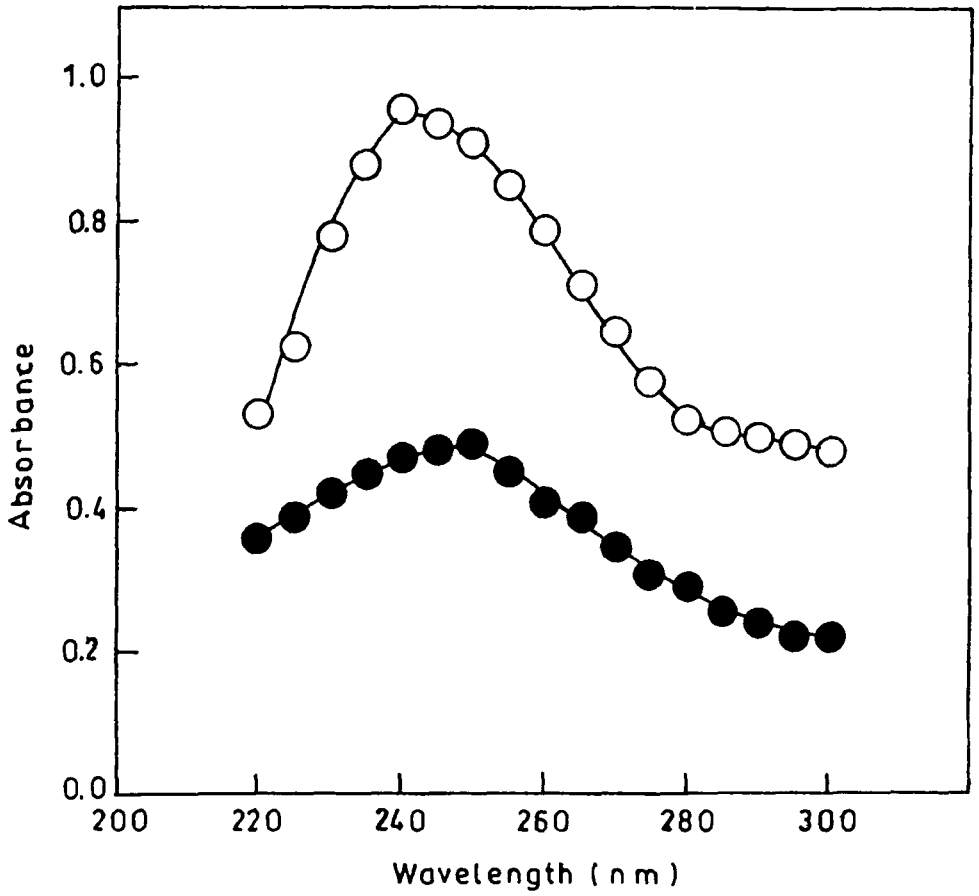


Figure 2.3 Absorption spectra of isoproturon (5.0×10^{-5} mol dm^{-3} in 0.1 mol dm^{-3} HCl), (○) before refluxing, (●) after refluxing for 2 hours.

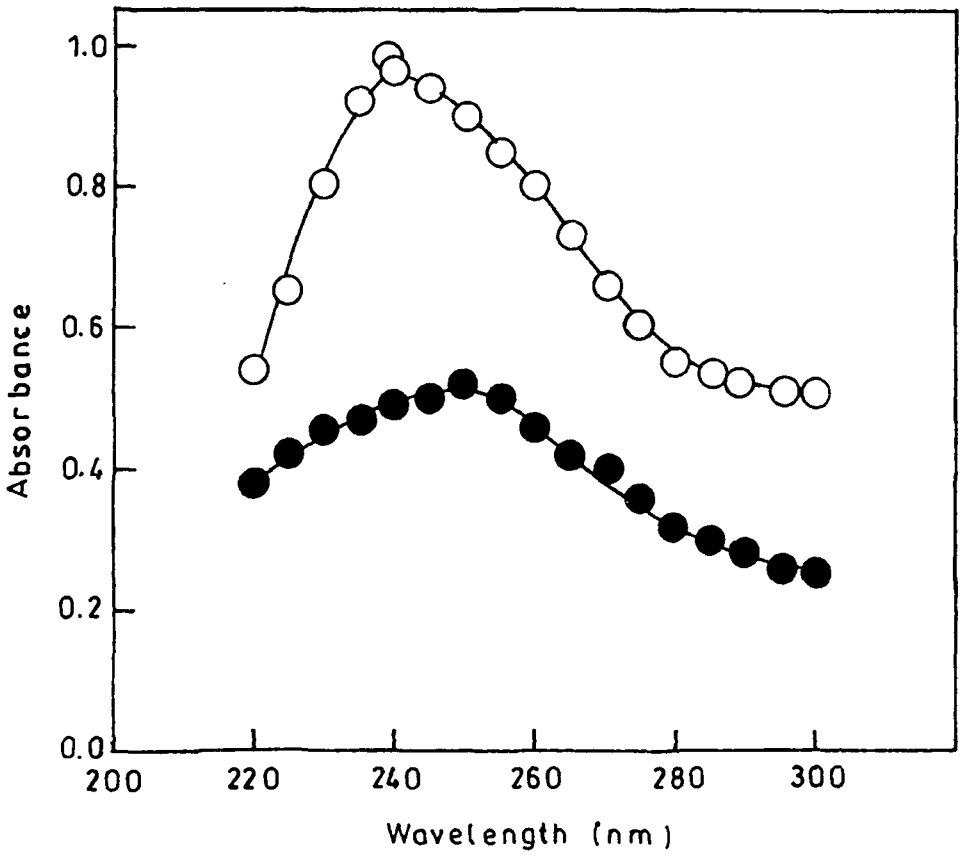


Figure 2.4 Absorption spectra of fenuron (5.0×10^{-5} mol dm^{-3} in 0.1 mol dm^{-3} HCl), (○) before refluxing, (●) after refluxing for 2 hours.

Chapter-3

Kinetics of Acidic Hydrolysis of Phenylureas in CTAB and NaLS Micelles

3.1 Results

3.1.1 Dependence of the Reaction Rate on [Phenylurea]

The order of the reaction with respect to phenylurea (isoproturon and fenuron) concentrations was obtained by carrying out experiments at different initial concentrations of phenylurea in the range from 4.0×10^{-5} to 10×10^{-5} mol dm^{-3}. The concentration of hydrochloric acid was kept constant at 0.1 mol dm^{-3}. The temperatures were fixed at 70°C and 80°C for isoproturon and fenuron respectively. The pseudo-first order rate constants were calculated by using computer program and are given in Tables 3.1-3.2 and in Figures 3.1-3.2.

To find out the dependence of the order of reaction on [phenylurea] in the presence of NaLS and CTAB surfactants, the studies were carried out in the presence of 2.0×10^{-2} and 1.0×10^{-2} mol dm^{-3} [surfactant] for isoproturon and fenuron, respectively. The remaining conditions of temperature and concentration of phenylurea and hydrochloric acid were the same as those of aqueous medium. The results are given in Tables 3.1 – 3.2 and are depicted graphically in Figures 3.1-3.2. It was observed that the values of rate constant were independent of the initial concentration of isoproturon and fenuron. Thus the order with respect of [phenylurea] is unity in both aqueous and micellar media.

3.1.2 Dependence of the Reaction Rate on [Hydrochloric Acid]

The rate constant dependence on hydrochloric acid concentration was determined by carrying out the kinetic

experiment at different concentrations of hydrochloric acid (=1.0×10^{-2} mol dm^{-3} – 1.0 mol dm^{-3}). The concentration of phenylurea was kept constant at 5.0×10^{-5} mol dm^{-3} at fixed temperature (70°C for isoproturon and 80°C for fenuron). The studies in the presence of micelles were carried out at [NaLS] (=2.0×10^{-2} mol dm^{-3} for isoproturon and 1.0×10^{-2} mol dm^{-3} for fenuron) and at [CTAB] (=2.0×10^{-2} mol dm^{-3} for isoproturon and 1.0×10^{-2} mol dm^{-3} for fenuron). The remaining conditions of temperature and concentration of reactants were the same as those for aqueous medium. The results are presented in Tables 3.3-3.4 and in Figures 3.3-3.4.

3.1.3 Dependence of the Reaction Rate on [Sodium Lauryl Sulfate]

The dependence of the observed pseudo first-order rate constant, k_ψ on NaLS concentration was investigated by carrying out a series of kinetic runs at different [NaLS] (= 5.0×10^{-4} – 5.0×10^{-2} mol dm^{-3}) with fixed concentrations of phenylurea (= 5.0×10^{-5} mol dm^{-3}) and HCl (=0.1 mol dm^{-3}) at 70°C (for isoproturon) and 80°C (for fenuron). The k_ψ values increased with increasing the [NaLS], reach to a maximum value and thereafter become almost constant. The results are summarized in Tables 3.5- 3.6 illustrated in Figures 3.5-3.6.

3.1.4 Dependence of the Reaction Rate on [Cetyltrimethylammonium Bromide]

The dependence of the observed k_ψ at different CTAB concentrations was investigated by carrying out a series of kinetic runs at [CTAB] in the range from 5.0×10^{-4} mol dm^{-3} to

6.0×10^{-2} mol dm^{-3} with fixed concentrations of phenylurea (=5.0 $\times10^{-5}$ mol dm^{-3}) and HCl (= 0.1 mol dm^{-3}) at 70°C (for isoproturon) and 80°C (for fenuron). The k_ψ values decreased continuously with increasing CTAB concentrations. The results are summarized in Tables 3.7-3.8 and shown graphically in Figures 3.7-3.8.

3.1.5 Dependence of the Reaction Rate on Temperature

Kinetic experiments were carried out at different temperatures (40°C-90°C) while the concentrations of phenylurea and HCl were kept constant at 5.0×10^{-5} mol dm^{-3} and 0.1 mol dm^{-3} respectively. The influence of temperature on the rate of hydrolytic reaction of phenylureas in the micellar media was studied at [NaLS] (= 2.0 $\times10^{-2}$ mol dm^{-3} for isoproturon and 1.0 $\times10^{-2}$ mol dm^{-3} for fenuron) and [CTAB] (= 2.0 $\times10^{-2}$ mol dm^{-3} for isoproturon and 1.0 $\times10^{-2}$ mol dm^{-3} for fenuron). The rate constants calculated at different temperatures are given in Tables 3.9- 3.10. Figures 3.9– 3.10 are the plots of log k_{obs} *versus* $\frac{1}{T}$ for the hydrolytic reaction of phenylurea in aqueous medium. The plots of log k_ψ *versus* $\frac{1}{T}$ for acidic hydrolytic reaction of phenylurea in micellar media are presented in Figures 3.11– 3.12.

The kinetic parameters, e.g., energy of activation, ΔE_a, standard enthalpy change, $\Delta H^{\#}$ and standard entropy change, $-\Delta S^{\#}$ were determined from the plot of k_{obs} versus $\frac{1}{T}$ and are given in Tables 3.9- 3.10.

3.1.6 Dependence of the Reaction Rate on [Salt]

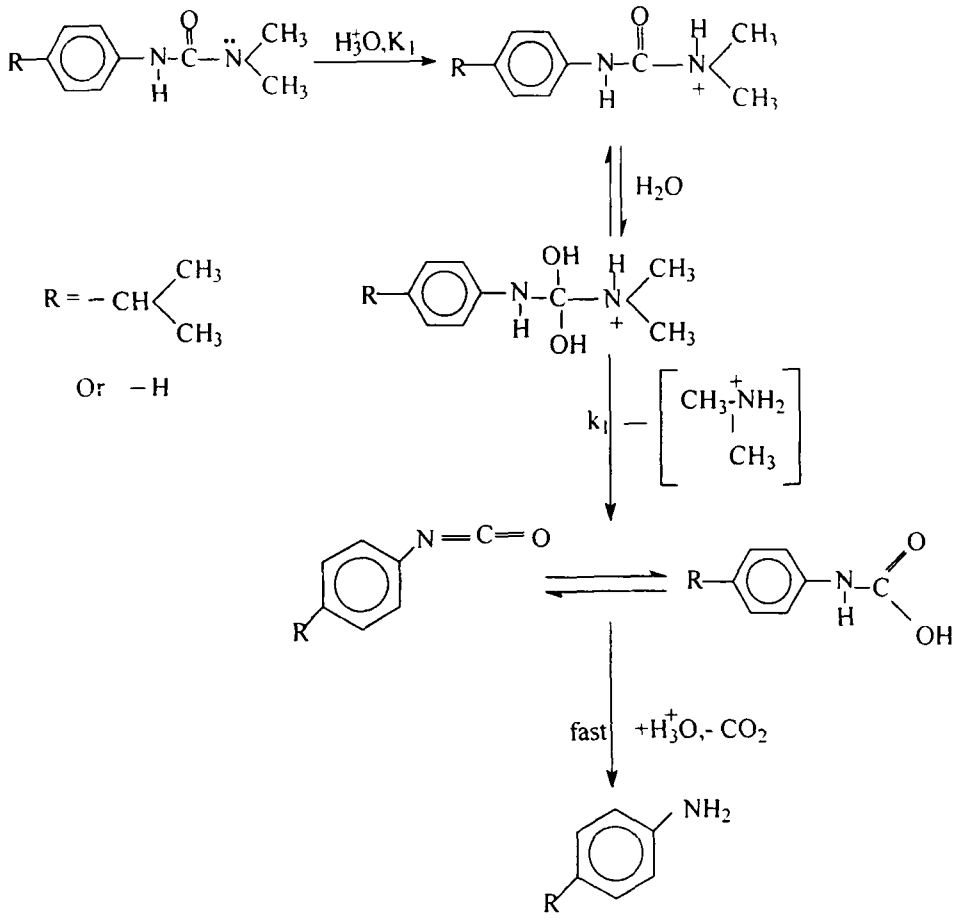
The effect of salts in presence and absence of NaLS and CTAB micelles were carried out at fixed concentrations of phenylurea (=5.0× 10^{-3} mol dm^{-3}), HCl (=0.1 mol dm^{-3}) and surfactant (=2.0 ×10^{-2} mol dm^{-3} for isoproturon and 1.0 ×10^{-2} mol dm^{-3} for fenuron). The temperatures were kept constant at 70°C for isoproturon and 80°C for fenuron. The added salts did not influence the values of the rate constant in aqueous medium while in the presence of surfactants, the values of rate constant decreased with the increasing [salt]. The results are given in Tables 3.11-3.12 and Figures 3.13-3.14.

3.2 Discussion

3.2.1 Reaction in Aqueous Medium

The observed results show that the rate of reaction is independent of the initial concentrations of phenylurea thereby indicating that the reaction follows first-order kinetics in [phenylurea]. The values of the rate constant rises with the increase in [HCl] in solutions of low acidity but becomes constant at higher [HCl]. A possible mechanism of the reaction is presented in Scheme 3.1.

The hydrolysis of phenylureas is initiated by the protonation of alkyl amino nitrogen.[118] After the protonation, phenylurea is then attacked by water to give tetrahedral intermediate. The attack by water is a rate determining step and the tetrahedral intermediate decompose to yield phenyl isocyanate and dimethyl amine. During reaction, water facilitate the intramolecular proton transfer from unprotonated or N-protonated phenylurea resulting the elimination of amine.[114] Thus, in the acidic medium, the hydrolysis of phenylureas proceeds through addition-elimination mechanism.



Scheme 3.1

The intermediate phenyl isocyanate is unstable and in acidic medium it yields another intermediate i.e., phenyl carbamic acid. Moodie and coworkers[124] reported a half life period of 20s for the hydrolysis of phenyl isocyanate in aqueous solution at 25^{0}C. In acidic solution, phenyl carbamic acid is very unstable and decarboxylates rapidly to give substituted aniline.

In the lower concentration range of hydrochloric acid, the amount of the N-protonated phenylurea increases with the increase in acidities and reaches to maximum.[125] Any further increase in acid concentration cause a decrease in concentration

of N-protonated phenylurea and favours the O-protonation. Giffney and Connor[114] concluded that N-protonated urea is the reactive entity while O-protonated conjugate acid does not decompose at low to intermediate acidities.

The rate limiting behavior at higher [HCl] can be explained by considering the protonation of phenylurea at carbonyl group which is non-reactive entity. An equilibrium exists between the O-protonated and N-protonated urea depending upon the acid concentration. The low acid concentration favours N-protonation and so the reaction is linearly dependent on [HCl] and at higher acid concentration O-protonation is favoured. The other factor which contributes towards the limiting values of rate constant at higher [HCl] is water activity. The attack on N-protonated urea by water is a rate determining step and the activity of water is reduced with the increase in acidities. Therefore, the rate of hydrolysis at higher [HCl] is decreased. Thus at higher [HCl] the lower activity of water play crucial role in the rate limiting behaviour of rate constant -[HCl] profile.

3.2.2 Reaction in Micellar Media

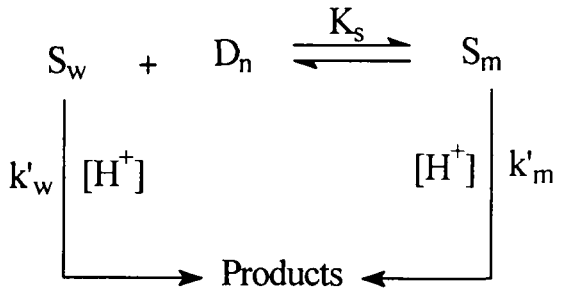
The rates of acidic hydrolysis of phenylureas were studied in presence of anionic NaLS and cationic CTAB micelles. It was observed that the absorption spectra of reactants and products were the same in aqueous and micellar media. This confirms that the reaction products in micellar media are the same as in aqueous medium. The similar behaviour in the dependence of the values of rate constants on [phenylurea] and [HCl] in aqueous and micellar media suggests that the pseudo-first order reaction

mechanism remains the same in presence of NaLS and CTAB micelles as that in aqueous medium with all possible intermediate situations. The rates of acidic hydrolysis of phenylureas are affected by the ionic micelles and the reactions under discussion follow this general pattern. The electrostatic and hydrophobic interactions between micelles and reactants, transition state, and products are involved in the micellar solutions. The micellar surface can attract or repel ionic species due to electrostatic interactions whereas hydrophobic interaction can bring about incorporation into micelles. The observed catalysis is due to the both the increased concentration of reactants in the Stern's layer and the stabilization of the product by the micelles.

The NaLS micelles concentrate both hydrogen ions and phenylurea into very small volume of Stern's layer. In acidic medium, the phenylurea is protonated and this positively charged phenylurea gets more strongly bonded to anionic NaLS micelles. Thus the micelle facilitates the extensive build up of protonated phenylurea in the region of Stern's layer and enhance the rate of hydrolysis. In the presence of micelles, the dependence of rate of hydrolysis is linear on [HCl] in lower concentration range but show a levelling behaviour at higher concentrations (Figures 3.3 - 3.4). This phenomenon may arise due to the low polarity of Stern's layer of micelles as compared to water. The studies by Giffney and O'Connor[114] demonstrate that the rate of hydrolysis of phenylurea increases with the acid strength at low acidity. It elaborates the role of water activity during the hydrolysis of phenylurea. The activity of water is reduced appreciably at higher acidity. The addition of water to the protonated

phenylurea (which is rate determining step) become slow in the Stern's layer.

The observed increase in rate of acidic hydrolysis of phenylurea upon addition of NaLS micelles can be explained on the basis of pseudophase kinetic model of micelles proposed by Megner and Portnoy[71] and developed by Bunton,[78] Romsted[126] and Vera and Rodenas.[127] The aqueous micelles are considered as submicroscopic reaction media and the reactants are distributed rapidly between water and micelles which are regarded as distinct reaction regions. The overall reaction rate is the sum of rates in the water and in the micelles. Thus the hydrolysis of phenylurea occurring in NaLS micelles can be presented by scheme 3.2



Scheme 3.2

In this scheme 'S' denotes phenylurea, D_n is the micellized surfactant (i.e., $[D_n]$ = [Total surfactant]-cmc) and K_S is the binding constant of phenylurea with NaLS micelles. Subscript w and m denotes aqueous and micellar pseudophases, respectively.

Corresponding to scheme 3.2 the overall rate constant in terms of first-order rate constant in aqueous (k'_w) and micellar (k'_m) pseudophase is derived as follows:

$$\frac{dp}{dt} = k_\psi[S_T] \qquad (3.1)$$

$$= k[H_T^+][S_T]$$

$$= k'_w[S_w] + k'_m[S_m] \qquad (3.2)$$

where $[H_T^+] = [H_m^+] + [H_w^+]$ (3.3)

$$K_S = \frac{[S_m]}{[S_w][D_n]} \qquad (3.4)$$

or $[S_m] = K_S[S_w][D_n]$ (3.5)

From equations (3.1) and (3.5), we get

$$\frac{dp}{dt} = k'_w[S_w] + k'_m K_S[S_w][D_n]$$

taking $[S_w]$ common :

$$\frac{dp}{dt} = [S_w](k'_w + k'_m K_S[D_n]) \qquad (3.6)$$

since $[S_T] = [S_w] + [S_m]$

Therefore

$$[S_T] = [S_w] + K_S[S_w][D_n]$$

or $$[S_w] = \frac{[S_T]}{1 + K_S[D_n]} \qquad (3.7)$$

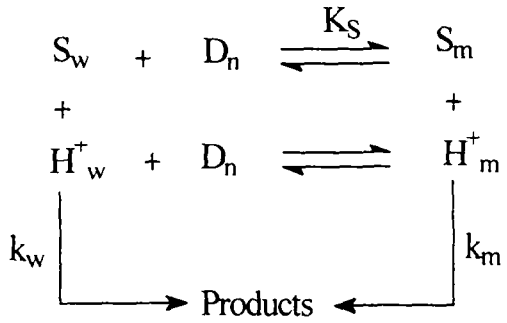
Thus equation (3.6) becomes

$$\frac{dp}{dt} = \frac{[S_T]}{1 + K_S[D_n]}(k'_w + k'_m K_S[D_n]) \qquad (3.8)$$

On comparison of equation (3.1) and (3.8); we get

$$k_{\psi} = \frac{k'_w + k'_m K_S [D_n]}{1 + K_S [D_n]} \qquad (3.9)$$

For a bimolecular reaction, the rate- [surfactant] profile can be treated quantitatively by taking into account the distribution of both reactants in water and in micelles. Therefore, the first order rate constant k'_w and k'_m can be expressed in terms of second order rate constant by considering the reactant concentrations in each aqueous and micellar pseudophases. The modified scheme can now be presented as follows:



Scheme 3.3

On the basis of scheme 3.3, the first-order rate equation (3.9) can be transformed in terms of second-order rate equation (3.10).

$$k_{\psi} = \frac{k_w [H^+_T] + (k_m K_s - k_w) m_{H^+} [D_n]}{1 + K_s [D_n]} \qquad (3.10)$$

where

$$k'_w = k_w [H^+_T] \qquad (3.11)$$

and $$k'_m = \frac{k_m [H^+_m]}{[D_n]} = k_m m_{H^+} \qquad (3.12)$$

k_m and k_w are second-order rate constants for reaction in micellar and aqueous pseudophases, respectively.

In micellar pseudophase, the ionic and polar reactants mainly occur in interfacial region called Stern's layer. The Stern's layer is highly aqueous and contains high concentration of ionic head groups and counter ions. Quantitatively the concentration of reactant counter ions (i.e. H^+) in the interfacial region is assumed to be that in the bulk water plus an increment predicted by the Pseudophase Ion Exchange (PIE) model developed by Romsted.[126] Romsted assumed that ions bind to micelles according the following equilibrium developed for ion exchange resin.

$$H^+_m + Na^+_w \underset{}{\overset{K_{H^+/Na^+}}{\rightleftharpoons}} H^+_w + Na^+_m \qquad (3.13)$$

The equilibrium constant for the exchange of H^+ and Na^+ at micellar surface is given by

$$K_{H^+/Na^+} = \frac{[Na^+_m][H^+_w]}{[Na^+_w][H^+_m]} \qquad (3.14)$$

The reactants exist in dynamic equilibrium between the aqueous and micellar pseudophases. The entrance and exit rates of phenylureas and H^+ from micelles are an order of magnitude faster than the rate of its hydrolysis. The distribution of surfactants, substrate, H^+ and counter ions, Na^+ are at thermodynamic equilibrium throughout the time course of reaction. On applying the mass balance for phenylurea, Na^+, H^+ and surfactant, the following quadratic equation was obtained for m_{II}^+

$$(m_{H^+})^2 + \left(\frac{[Na^+_T]+[H^+_w]}{[D_n]} - \beta\right)m_{H^+} - \frac{\beta[H^+_w]}{[D_n]} = 0 \qquad (3.15)$$

Where β is the degree of binding of counter ion by the micellar surface and $[H^+_w]$ was obtained from the measured pH ($pH = -\log [H^+_w]$).

Upon solving the quadratic equation (3.15), the value of m_H^+ can be obtained and the fitting values of k_m, K_S and $K_H^+/_{Na}^+$ were evaluated from the computer program by minimizing the deviation between the simulation and observed values for the k_ψ - [surfactant] profile. The values of these parameter are given in Tables 3.13 - 3.14.

The rate enhancement of bimolecular reactions are ascribed largely to increase in concentration of reactants in the small volume of the association colloids. Addition of surfactant lead to binding of both reactants to micelles and this increased concentration increases the overall reaction rate. But on comparing the second-order rate constant in micellar pseudophase to that in water, it is observed that the actual value of rate constant in micellar pseudophase is smaller than in water.

$$k_2^m = V_m k_m \quad \text{and} \quad k_2^m / k_w = 0.0524$$

where, V_m is the molar volume of NaLS micelles[128] and its value is 0.14 $dm^3\ mol^{-1}$

The lower value of rate constant in the micellar pseduophase may be attributed to the lower polarity of micellar surface and strong binding of hydrophilic H_3O^+ to anionic, NaLS micelles. Again, bulk water is better hydrogen bond donor than

the Stern's layer of micellar interface and therefore, results in lowering of reaction rate. The activity of water at the surface of NaLS micelles is ~ 0.6[129] and thus it also contributes towards lowering of k_2^m value for the acidic hydrolysis of phenylureas.

In acidic medium, phenylureas is protonated and is positively charged. The micelles bind polar and ionic organic molecules at their surface in the Stern layer and the extent of binding (K_S) depend upon the hydrophobicity of substrate. The value of K_S(=410 for isoproturon at 70°C and = 400 for fenuron at 80°C) is indicative of the strong association between the anionic, NaLS micelles and the hydrophobic phenylureas. The lower binding constant for fenuron as compared to isoproturon may be due to higher temperature and lower hydrophobicity. The presence of isopropyl group in isoproturon makes it more hydrophobic.

The observed decrease in reaction rate in the presence of salt can be explained on the basis of coulumbic interactions between micelles and ions. The extent of ion transfer between water and micellar surface or the ionic concentrations in the association colloids influence the reactivity. The competition between the inert ions i.e., (K^+ and Na^+) and reactive H^+ ions take place for binding at NaLS micelles.[130-132] The low charge density ions displace the high charge density hydrophilic ions from the micellar surfaces. Therefore, the addition of Na^+ and K^+ causes a displacement of H^+ from the micellar surface and results in the decreased reaction rate. The presence of low charge density ions and co-ions on the micellar surface results in the

greater extent of binding of hydrophobic phenylurea with anionic and cationic micellar surface. Thus apart from the exclusion of H^+ from the micellar surface, the added electrolyte also cause micelles to grow and change their shape and influence the reactivity.

An attempt was made to see the effect of cationic, CTAB micelles on the acidic hydrolysis of phenylurea at constant [phenylurea] (= 5.0×10^{-5} mol dm^{-3}), [HCl] (= 0.1 mol dm^{-3}) and fixed temperature (Figures 3.7-3.8). A continuous inhibition in rate of hydrolysis of phenylurea by HCl in the presence of cationic, CTAB micelles was observed. The pseudophase model explains the micellar inhibition of bimolecular reactions of co-ions in terms of incorporation of organic substrate and exclusion of reactive ion. The acidic hydrolysis of phenylurea is not completely suppressed by CTAB micelles because of the presence of very small concentrations of H^+ and N-protonated phenylurea at the micellar surface as co-ions. The concentration gradient of co-ions between water and the interface region is very large with dilute co-ions, but it decreases as total concentration is increased. Thus under the condition of high concentration of co-ions, the concentration gradients disappear between the aqueous and the interfacial region and the inhibition reaction is decreased significantly as the total co-ions concentration is increased.[133] The coulumbic model also predicts that there will be a small but finite concentration of co-ions at micellar surfaces. The residual hydrolysis of phenylureas by HCl at CTAB micellar surface is considered to be very small and negligible as compared the

reaction rate in aqueous pseudophase. Thus the observed rate of reaction is due to the reaction occurring in aqueous pseudophase. The terms k_m and m_{H^+} in equation (3.10) is assumed to be negligible and the rate equation can be written as

$$k_\psi = \frac{k_w [H_T^+]}{1 + K_S [D_n]} \qquad (3.16)$$

$$\text{or} \quad \frac{k_w [H_T^+]}{k_\psi} = 1 + K_S [D_n] \qquad (3.17)$$

A plot of $\frac{k_w [H_T^+]}{k_\psi}$ versus $[D_n]$ (as shown in Figure 3.15-3.16) gave a straight line with the slope K_S (= 24.31 for isoproturon and 28.82 for fenuron). The smaller value of K_S is an indicative of weak binding between cationic CTAB micelles and hydrophobic phenylureas.

The effect of temperature on the rate constant for the hydrolysis of phenylureas with hydrochloric acid in presence of surfactants was used to evaluate activation parameters. The activation parameters were evaluated from linear regression of log k_{obs} versus $\frac{1}{T}$ (for aqueous medium) and log k_ψ versus $\frac{1}{T}$ (for micellar media) by least square method.

The enthalpy and entropy of activation were calculated by using Eyring relationship.[134] Lowering in ΔE_a in presence of micelles in comparison with aqueous medium suggests that the reaction proceeds through some other path which has lower energy of activation. Similarly the increase in E_a favours the path of higher energy of activation. The decrease in entropy suggests

a greater degree of orderliness while an increase in entropy shows greater degree of randomness during the transition of reactant into products. The rate constant increases on increasing the temperature is due to interaction of phenylurea with micelles favour the charge dispersion of phenylurea in transition state and its greater degree of orderliness results in the increase in the value of rate constants.

The added salts (NaCl, KCl or KNO_3) inhibited the reaction rate and the values of pseudo-first order rate constant were decreased as shown in Tables 3.11-3.12 and in Figures 3.13 - 3.14. The inhibition effect could be due to a competitive binding of H^+ and Na^+ / K^+ counter ions with the micelles. The added salts also cause micelles to grow and change their shapes from spherical to spheroidal or rod-like. Its results into change in reaction rate at micellar surface.[135-137]

Table. 3.1

Effect of variation of [Isoproturon] on rate constants in the aqueous (k_{obs}) and in presence of CTAB and NaLS micelles (k_{ψ}) for acidic hydrolytic reaction of isoproturon.

Reaction conditions:

[Isoproturon] = 5.0×10^{-5} mol dm^{-3}

[HCl] = 0.1 mol dm^{-3}

Temperature = 70°C

10^5 [Isoproturon] (mol dm^{-3})	Rate Constants		
	Aqueous $10^5 k_{obs}$ (s^{-1})	CTAB $10^5 k_{\psi}$ (s^{-1})	NaLS $10^5 k_{\psi}$ (s^{-1})
4.0	8.56±0.22	5.42±0.17	15.55±0.37
5.0	8.66±0.24	5.51±0.18	15.64±0.39
6.0	8.71±0.21	5.59±0.16	15.63±0.41
8.0	8.87±0.23	5.64±0.14	15.69±0.38
10.0	8.91±0.25	5.71±0.17	15.79±0.40

[CTAB] = 2.0×10^{-2} mol dm^{-3}

[NaLS] = 2.0×10^{-2} mol dm^{-3}

Table. 3.2

Effect of variation of [Fenuron] on rate constants in the aqueous (k_{obs}) and in presence of CTAB and NaLS micelles (k_{ψ}) for acidic hydrolytic reaction of fenuron.

Reaction conditions:

[Fenuron] = 5.0×10^{-5} mol dm^{-3}

[HCl] = 0.1 mol dm^{-3}

Temperature = 80°C

10^5 [Fenuron] (mol dm^{-3})	Rate Constants		
	Aqueous $10^5 k_{obs}$ (s^{-1})	CTAB $10^5 k_{\psi}$ (s^{-1})	NaLS $10^5 k_{\psi}$ (s^{-1})
4.0	4.94±0.20	3.84±0.16	6.81±0.19
5.0	5.11±0.19	3.95±0.17	6.93±0.20
6.0	5.16±0.21	4.01±0.19	6.99±0.17
8.0	5.24±0.22	4.07±0.20	7.06±0.18
10.0	5.29±0.22	4.11±0.21	7.10±0.21

[CTAB] = 1.0×10^{-2} mol dm^{-3}

[NaLS] = 1.0×10^{-2} mol dm^{-3}

Table. 3.3

Effect of variation of [HCl] on rate constants in the aqueous(k_{obs})and in presence of CTAB and NaLS micelles(k_{ψ}) for the acidic hydrolytic reaction of isoproturon.

Reaction conditions:

[Isoproturon] = 5.0×10^{-5} mol dm^{-3}

Temperature = 70°C

[HCl] (mol dm^{-3})	Rate Constants		
	Aqueous $10^5 k_{obs}$ (s^{-1})	CTAB $10^5 k_{\psi}$ (s^{-1})	NaLS $10^5 k_{\psi}$ (s^{-1})
0.05	7.89±0.20	4.50±0.11	14.08±0.28
0.1	8.58±0.22	5.54±0.13	15.94±0.32
0.2	10.55±0.25	6.18±0.14	18.36±0.36
0.3	11.81±0.24	6.43±0.16	20.02±0.42
0.4	13.18±0.26	6.62±0.15	22.11±0.48
0.5	14.23±0.30	6.73±0.18	23.04±0.53
1.0	15.61±0.31	6.84±0.19	24.36±0.62

[CTAB] = 2.0×10^{-2} mol dm^{-3}

[NaLS] = 2.0×10^{-2} mol dm^{-3}

Table. 3.4

Effect of variation of [HCl] on rate constants in the aqueous (k_{obs}) and in presence of CTAB and NaLS micelles (k_{ψ})for the acidic hydrolytic reaction of fenuron.

Reaction conditions:

[Fenuron] = 5.0×10^{-5} mol dm^{-3}

Temperature = 80°C

[HCl] (mol dm^{-3})	Rate Constants		
	Aqueous $10^5 k_{obs}$ (s^{-1})	CTAB $10^5 k_{\psi}$ (s^{-1})	NaLS $10^5 k_{\psi}$ (s^{-1})
0.01	2.44±0.06	2.11±0.04	3.89±0.12
0.02	3.48±0.10	3.08±0.08	5.42±0.20
0.05	4.73±0.19	3.66±0.11	6.28±0.19
0.1	5.06±0.18	3.96±0.14	6.93±0.21
0.2	5.26±0.20	4.43±0.17	7.16±0.25
0.3	5.43±0.21	4.49±0.16	7.38±0.28
0.5	5.54±0.16	4.57±0.15	7.46±0.23
0.8	5.32±0.18	4.61±0.18	7.50±0.24
1.0	5.27±0.21	4.64±0.14	7.53±0.22

[CTAB] = 1.0×10^{-2} mol dm^{-3}

[NaLS] = 1.0×10^{-2} mol dm^{-3}

Table. 3.5

Effect of variation of [NaLS] on rate constants (k_ψ) for the acidic hydrolytic reaction of isoproturon.

Reaction conditions:

[Isoproturon] = 5.0×10^{-5} mol dm^{-3}

[HCl] = 0.1 mol dm^{-3}

Temperature = 70°C

10^3 [NaLS] (mol dm^{-3})	Rate Constants
	10^5 k_ψ (s^{-1})
0.0	8.66±0.22
0.5	9.01±0.23
1.0	9.30±0.20
2.0	9.69±0.21
5.0	11.0±0.24
10.0	13.56±0.27
20.0	15.94±0.30
30.0	17.40±0.32
40.0	17.86±0.34
50.0	17.96±0.38

Table. 3.6

Effect of variation of [NaLS] on rate constants (k_ψ) for the acidic hydrolytic reaction of fenuron.

Reaction conditions:

[Fenuron] = 5.0×10^{-5} mol dm^{-3}

[HCl] = 0.1 mol dm^{-3}

Temperature = 80°C

10^3 [NaLS] (mol dm^{-3})	Rate Constants
	$10^5 k_\psi$ (s^{-1})
0.0	5.06±0.14
0.5	5.16±0.16
1.0	5.48±0.15
2.0	5.83±0.18
5.0	6.28±0.18
10.0	6.93±0.17
20.0	7.36±0.15
30.0	7.67±0.18
40.0	7.89±0.19
50.0	7.96±0.20
60.0	8.02±0.22

Table. 3.7

Effect of variation of [CTAB] on rate constants (k_ψ) for the acidic hydrolytic reaction of isoproturon.

Reaction conditions:

[Isoproturon] = 5.0×10^{-5} mol dm^{-3}

[HCl] = 0.1 mol dm^{-3}

Temperature = 70°C

10^3 [CTAB] (mol dm^{-3})	**Rate Constants 10^5 k_ψ (s^{-1})**
0.0	8.66±0.23
0.5	8.47±0.20
1.0	8.29±0.25
2.0	8.01±0.24
5.0	7.49±0.23
10.0	6.70±0.20
20.0	5.54±0.18
30.0	4.60±0.16
40.0	4.01±0.14
50.0	3.72±0.11
60.0	3.64±0.10

Table. 3.8

Effect of variation of [CTAB] on rate constants (k_ψ) for the acidic hydrolytic reaction of fenuron.

Reaction conditions:

[Fenuron] = 5.0×10^{-5} mol dm^{-3}

[HCl] = 0.1 mol dm^{-3}

Temperature = 80°C

10^3 [CTAB] (mol dm^{-3})	Rate Constants $10^5 k_\psi$ (s^{-1})
0.0	5.06±0.21
0.5	4.95±0.17
1.0	4.68±0.20
2.0	4.43±0.21
5.0	4.21±0.23
10.0	3.95±0.18
20.0	3.16±0.15
30.0	2.52±0.12
40.0	2.13±0.10
50.0	1.98±0.08
60.0	1.92±0.06

Table. 3.9

Effect of variation of temperature on rate constants in the aqueous (k_{obs}) and in presence of CTAB and NaLS micelles (k_ψ) for the acidic hydrolytic reaction of isoproturon.

Reaction conditions:

[Isoproturon] = 5.0×10^{-5} mol dm^{-3}

[HCl] = 0.1 mol dm^{-3}

Temperature (°C)	Rate Constants		
	Aqueous $10^5 k_{obs}$ (s^{-1})	CTAB $10^5 k_\psi$ (s^{-1})	NaLS $10^5 k_\psi$ (s^{-1})
40	5.43±0.22	2.82±0.09	5.24±0.19
50	6.13±0.25	3.72±0.12	7.73±0.26
60	7.33±0.30	4.62±0.18	11.60±0.35
70	8.57±0.36	5.54±0.20	15.94±0.42
80	9.85±0.40	7.80±0.27	18.90±0.60
Activation Parameters			
E_a (kJ mol^{-1})	14.01±1.23	22.32±1.44	30.16±1.61
$\Delta H^{\#}$ (kJ mol^{-1})	11.53±1.62	19.85±1.10	27.67±1.74
$-\Delta S^{\#}$ (JK^{-1} mol^{-1})	284.01±4.01	219.07±5.32	225.06±6.00.

[CTAB] = 2.0×10^{-2} mol dm^{-3}

[NaLS] = 2.0×10^{-2} mol dm^{-3}

Table. 3.10

Effect of variation of temperature on rate constants in the aqueous (k_{obs}) and in presence of CTAB and NaLS micelles (k_ψ) for the acidic hydrolytic reaction of fenuron

Reaction conditions:

[Fenuron] = 5.0×10^{-5} mol dm^{-3}

[HCl] = 0.1 mol dm^{-3}

Temperature (°C)	Rate Constants		
	Aqueous $10^5 k_{obs}$ (s^{-1})	CTAB $10^5 k_\psi$ (s^{-1})	NaLS $10^5 k_\psi$ (s^{-1})
50	2.01±0.08	1.67±0.09	3.89±0.12
60	2.84±0.12	2.42±0.11	4.11±0.15
70	3.96±0.14	3.31±0.14	5.44±0.18
80	5.06±0.17	3.96±0.18	6.93±0.21
90	9.64±0.21	6.09±0.19	12.49±0.28
Activation Parameters			
E_a (kJ mol^{-1})	36.05±2.42	31.28±1.76	27.32±2.11
$\Delta H^{\#}$ (kJ mol^{-1})	33.58±2.51	28.81±2.12	24.84±1.60
$-\Delta S^{\#}$ (JK^{-1} mol^{-1})	215.87±6.30	234.25±4.26	242.56±8.81

[CTAB] = 1.0×10^{-2} mol dm^{-3}

[NaLS] = 1.0×10^{-2} mol dm^{-3}

Table. 3.11

Effect of variation of inorganic salts on rate constants in the presence of CTAB and NaLS micelles (k_ψ) for the acidic hydrolytic reaction of isoproturon.

Reaction conditions:

[Isoproturon] = 5.0×10^{-5} mol dm^{-3}

[HCl] = 0.1 mol dm^{-3}

Temperature = 70°C

10^2 [salts] (mol dm^{-3})	Rate Constants			
	$10^5 k_\psi$ (s^{-1})			
	in CTAB		in NaLS	
	NaCl	KCl	NaCl	KCl
0.0	5.52±0.20	5.52±0.20	16.04±0.39	16.04±0.39
1.0	4.82±0.16	5.09±0.22	13.79±0.32	15.47±0.41
2.0	4.09±0.14	4.70±0.24	12.52±0.28	14.52±0.36
5.0	3.12±0.11	4.29±0.21	11.27±0.25	13.74±0.31
10.0	2.42±0.08	3.93±0.15	9.06±0.20	10.81±0.24
15.0	2.07±0.10	3.62±0.12	6.78±0.16	7.71±0.19
20.0	1.84±0.07	3.34±0.09	3.54±0.14	5.23±0.14

[CTAB] = 2.0×10^{-2} mol dm^{-3}

[NaLS] = 2.0×10^{-2} mol dm^{-3}

Table. 3.12

Effect of variation of inorganic salts on rate constants in the presence of CTAB and NaLS micelles (k_ψ) for the acidic hydrolytic reaction of fenuron.

Reaction conditions:

[Fenuron] = 5.0×10^{-5} mol dm^{-3}

[HCl] = 0.1 mol dm^{-3}

Temperature = 80°C

10^2 [salts] (mol dm^{-3})	Rate Constants			
	$10^5 k_\psi$ (s^{-1})			
	in CTAB		in NaLS	
	NaCl	KNO_3	NaCl	KNO_3
0.0	3.96±0.17	3.96±0.17	6.93±0.22	6.93±0.22
0.5	3.06±0.19	3.24±0.20	5.89±0.24	5.72±0.27
1.0	2.71±0.16	2.98±0.11	5.58±0.20	5.72±0.24
2.0	2.33±0.11	2.74±0.10	5.11±0.18	5.33±0.19
5.0	1.64±0.09	2.54±0.08	4.03±0.14	5.12±0.21
10.0	1.23±0.08	2.37±0.07	3.12±0.12	4.69±0.15
15.0	1.02±0.10	2.22±0.16	2.63±0.09	4.36±0.12
20.0	0.92±0.04	2.08±0.13	2.34±0.08	4.28±0.10

[CTAB] = 1.0×10^{-2} mol dm^{-3}

[NaLS] = 1.0×10^{-2} mol dm^{-3}

Table. 3.13

Values of rate parameters used to simulate k_ψ - [surfactant] profile and binding constant for the acidic hydrolytic reaction of isoproturon in NaLS and CTAB micelles.

Reaction conditions:

[Isoproturon] = 5.0×10^{-5} mol dm^{-3}

[HCl] = 0.1 mol dm^{-3}

Temperature = 70°C

Parameters and Constants	Values in NaLS	Values in CTAB
K_s (mol^{-1} dm^3)	410.00	24.31
k_m (mol^{-1} dm^3 s^{-1})	$2.43 \pm 0.19 \times 10^{-4}$	-
β	0.75	-
$K_{H^+ Na^+}$	1.00	-
cmc (mol dm^{-3})	8.36×10^{-3}	8.02×10^{-4}

Table. 3.14

Values of rate parameters used to simulate k_ψ-[surfactant] profile and binding constant for the acidic hydrolytic reaction of fenuron in NaLS and CTAB micelles

Reaction conditions:

[Fenuron] = 5.0×10^{-5} mol dm^{-3}

[HCl] = 0.1 mol dm^{-3}

Temperature = 80°C

Parameters and Constants	Values in NaLS	Values in CTAB
K_s (mol^{-1} dm^3)	400.00	28.82
k_m (mol^{-1} dm^3 s^{-1})	$1.41 \pm 0.11 \times 10^{-4}$	-
β	0.75	-
K_{H^+/Na^+}	1.00	-
cmc (mol dm^{-3})	8.64×10^{-3}	8.52×10^{-4}

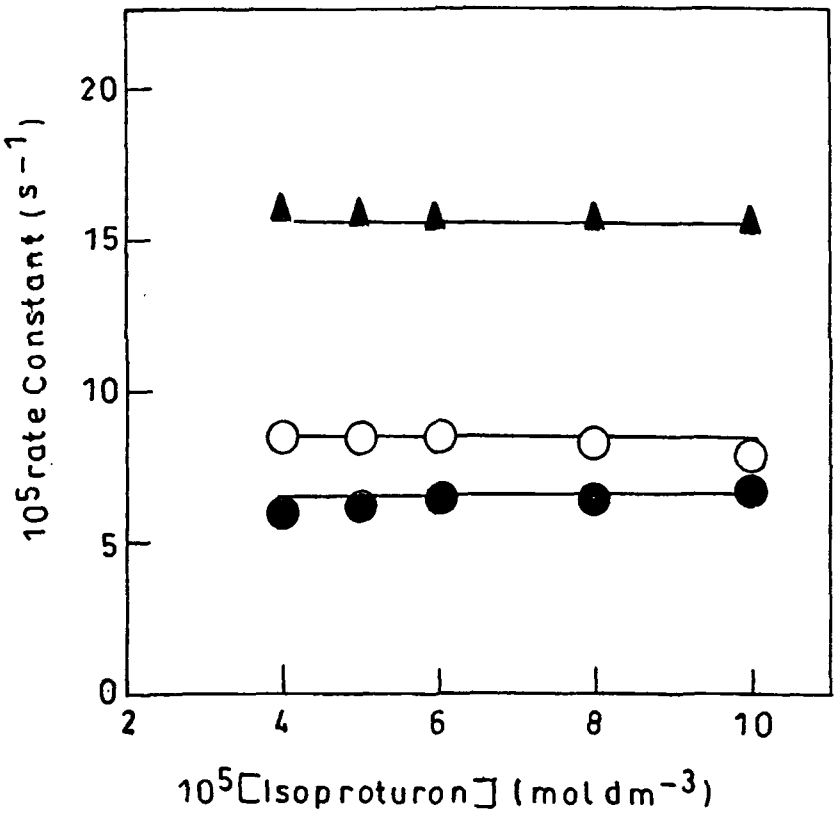


Figure 3.1 Effect of variation of [Isoproturon] on the values of rate constant in (o) aqueous, (•) CTAB and (▲) NaLS media.

Reaction Conditions: [HCl] = 0.1 mol dm^{-3}; [CTAB] =2.0 × 10^{-2} mol dm^{-3} and [NaLS] =2.0×10^{-2} mol dm^{-3} at 70°C.

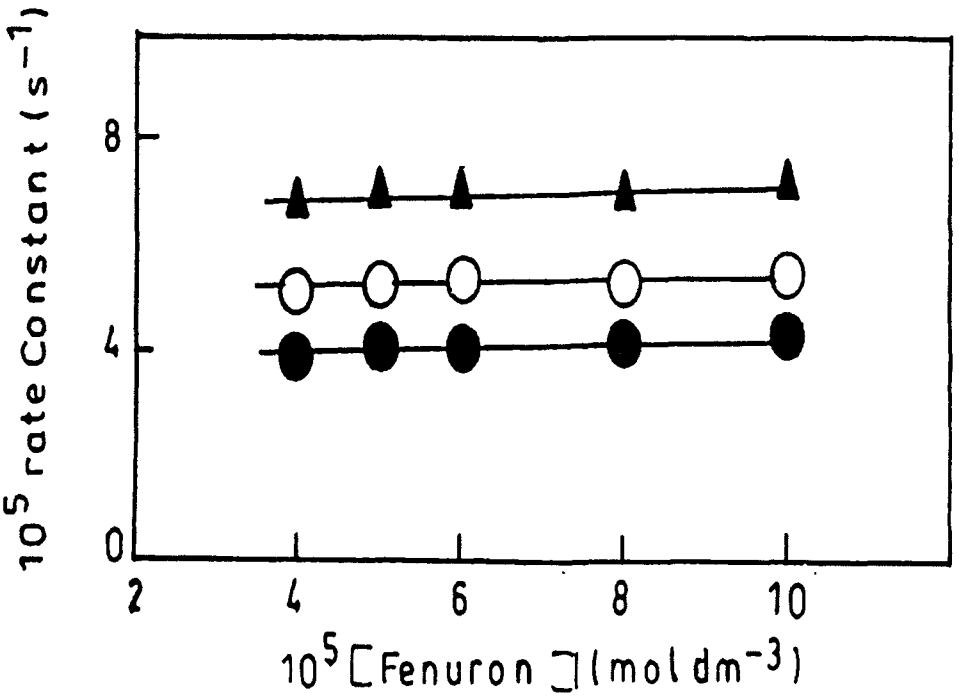


Figure 3.2 Effect of variation of [Fenuron] on the values of rate constant in (o) aqueous, (•) CTAB and (▲) NaLS media.

Reaction Conditions: [HCl] = 0.1 mol dm^{-3}; [CTAB] =1.0 × 10^{-2} mol dm^{-3} and [NaLS] =1.0×10^{-2} mol dm^{-3} at 80°C.

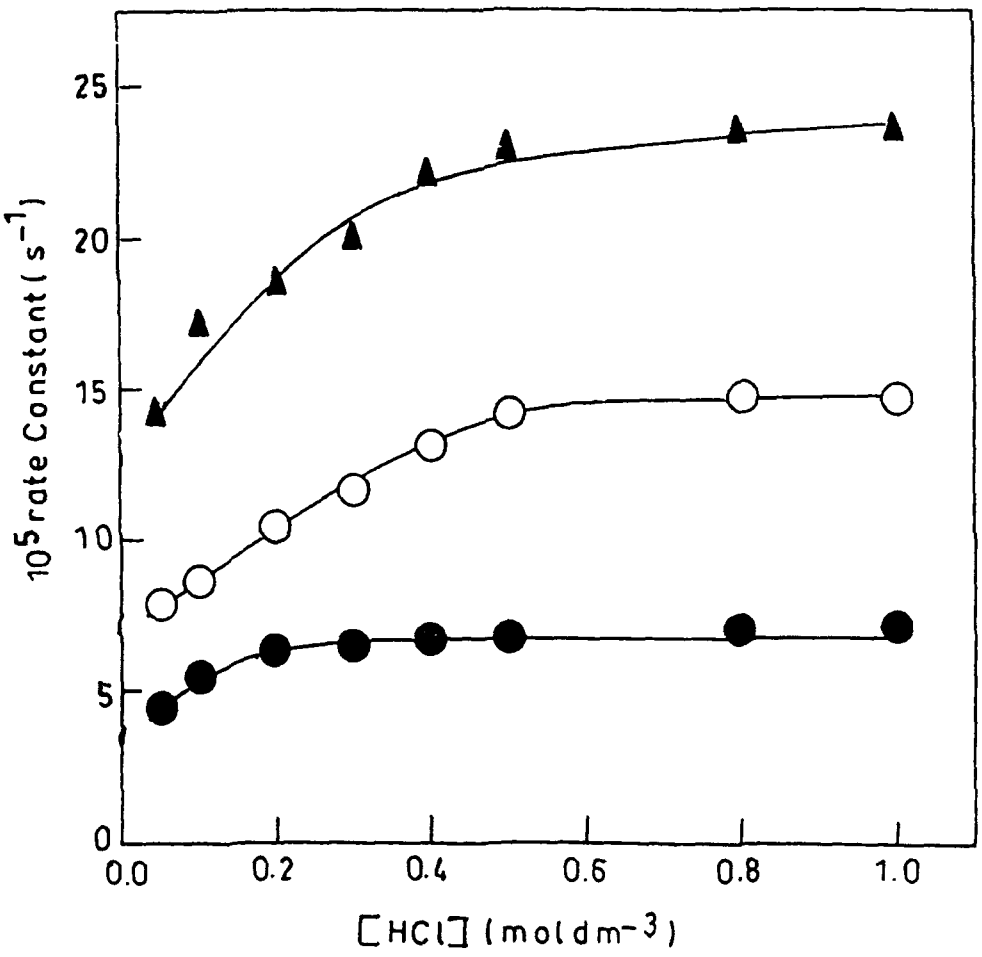


Figure 3.3 Effect of variation of [HCl] on the values of rate constant in (o) aqueous, (•) CTAB and (▲) NaLS media.

Reaction Conditions: [Isoproturon] = 5.0×10^{-5} mol dm^{-3}; [CTAB] =2.0×10^{-2} mol dm^{-3} and [NaLS] = 2.0×10^{-2} mol dm^{-3} at 70°C.

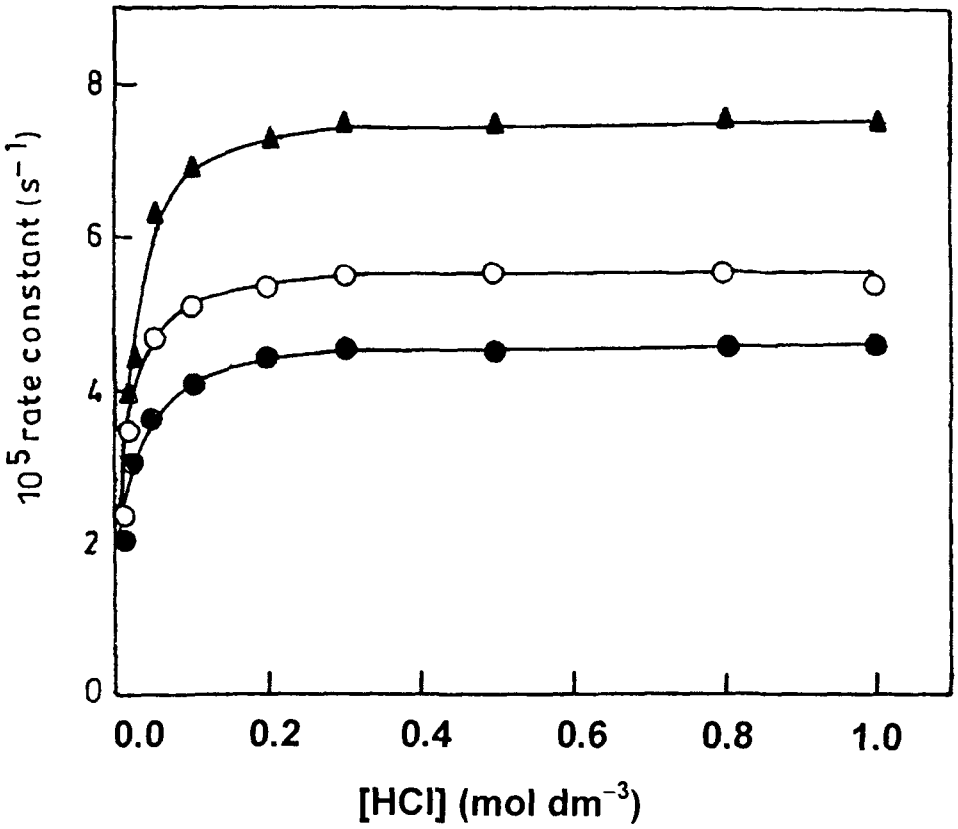


Figure 3.4 Effect of variation of [HCl] on the values of rate constant in (o) aqueous, (•) CTAB and (▲) NaLS media.

Reaction Conditions: [Fenuron] = 5.0×10^{-5} mol dm^{-3}; [CTAB] =1.0×10^{-2} mol dm^{-3} and [NaLS] =1.0×10^{-2} mol dm^{-3} at 80°C.

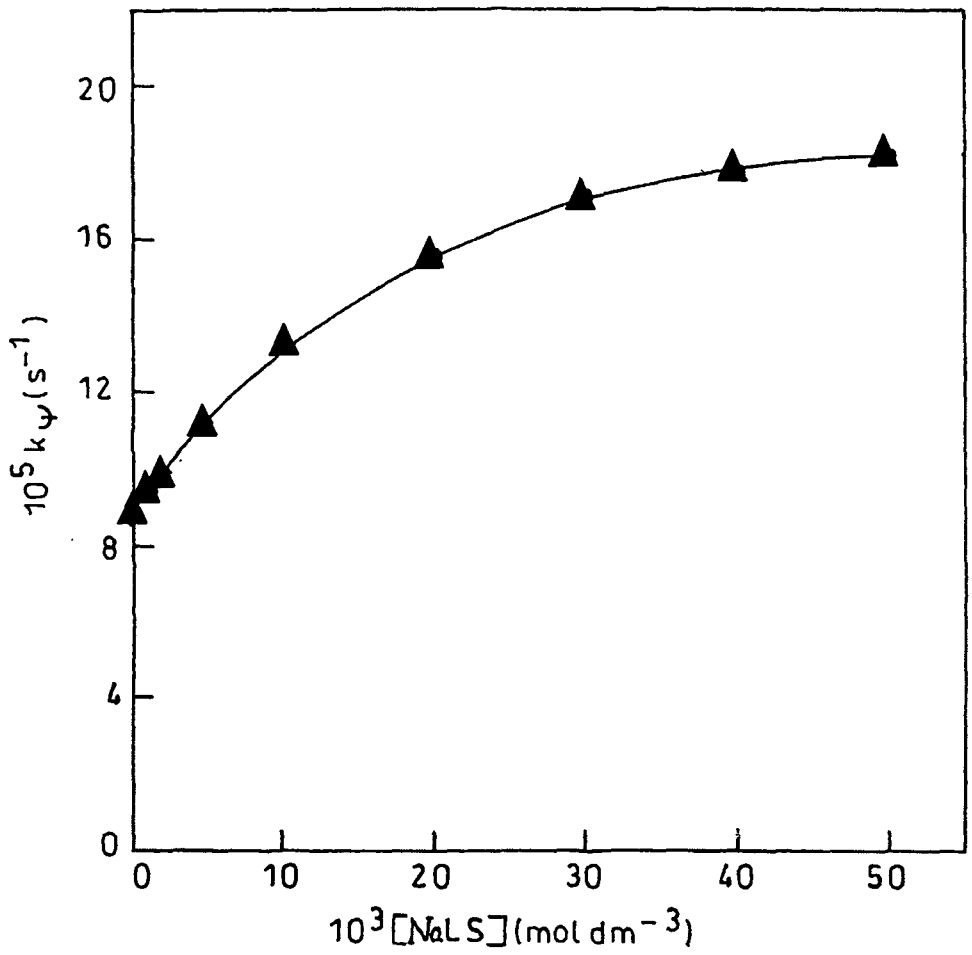


Figure 3.5 Effect of variation of [NaLS] on the values of rate constant (k_ψ).

Reaction Conditions: [Isoproturon] = 5.0×10^{-5} mol dm^{-3} and [HCl] =0.1 mol dm^{-3} at 70°C.

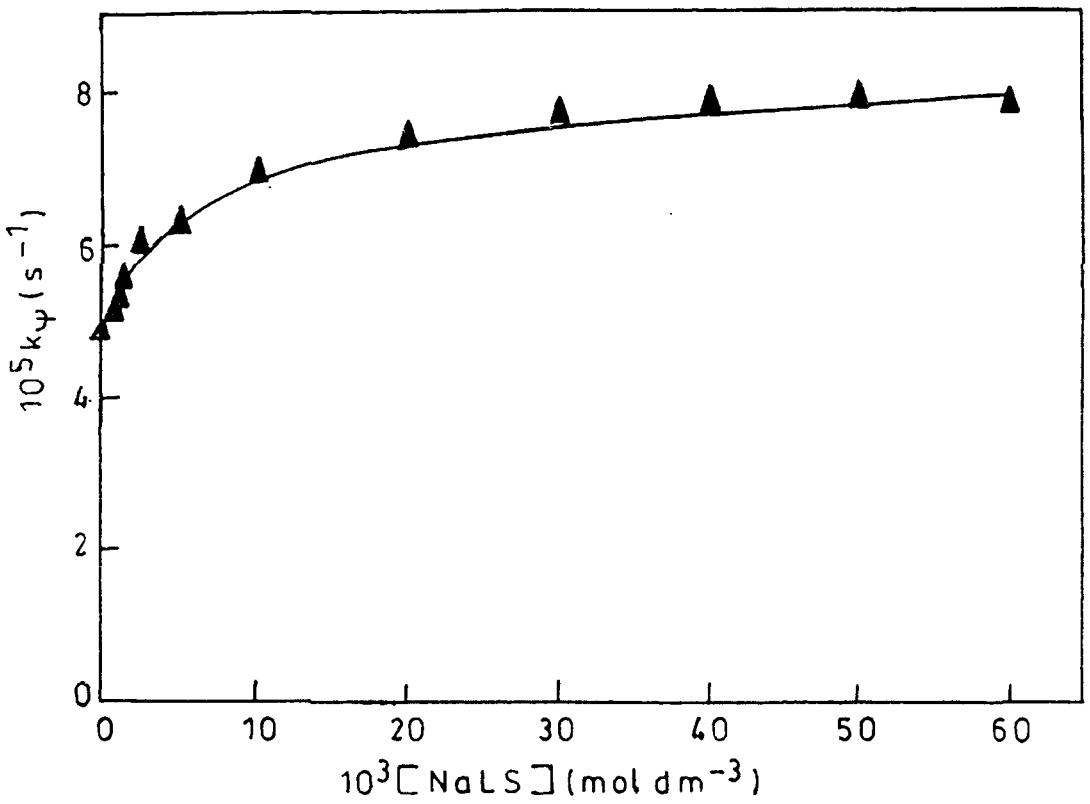


Figure 3.6 Effect of variation of [NaLS] on the values of rate constant (k_ψ).

Reaction Conditions: [Fenuron] = 5.0×10^{-5} mol dm^{-3} and [HCl] =0.1 mol dm^{-3} at 80°C.

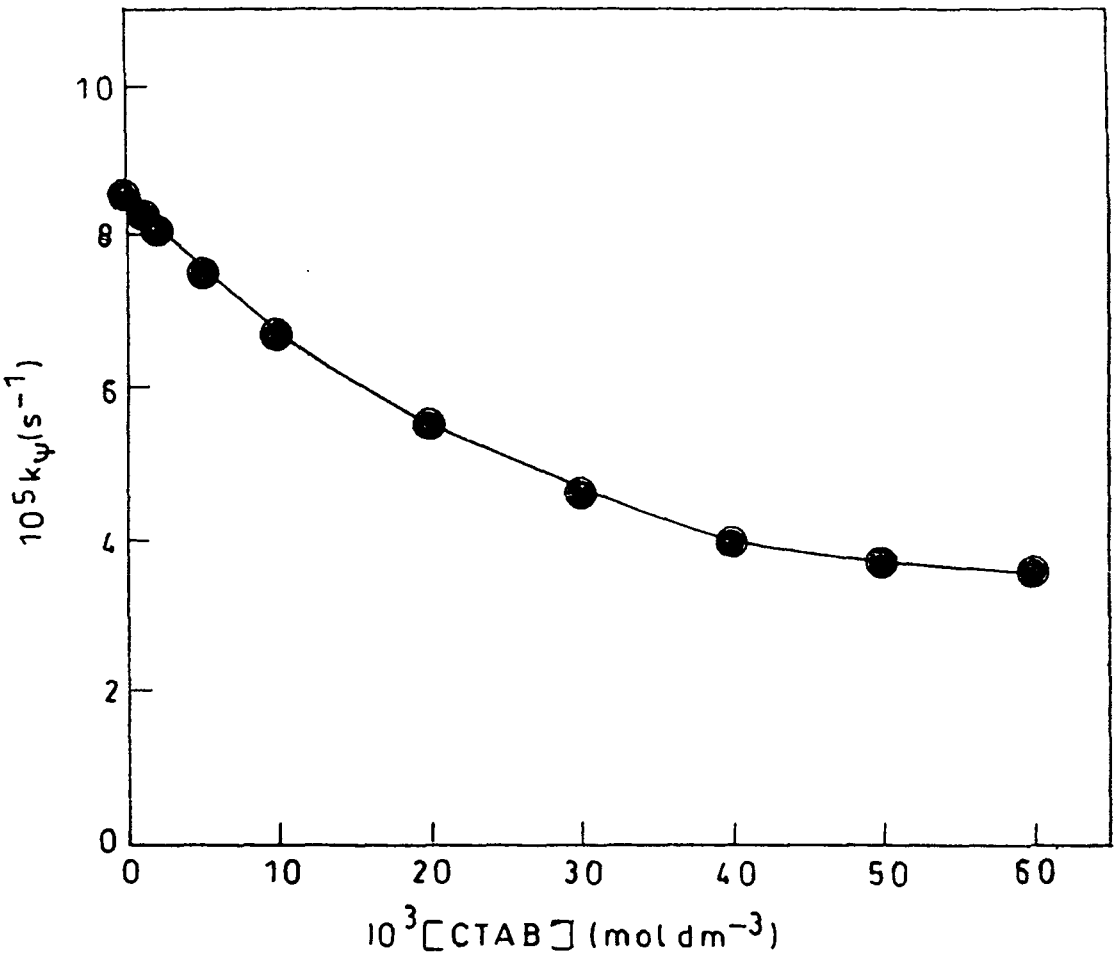


Figure 3.7 Effect of variation of [CTAB] on the values of rate constant (k_ψ).

Reaction Conditions: [Isoproturon] = 5.0×10^{-5} mol dm^{-3} and [HCl] =0.1 mol dm^{-3} at 70°C.

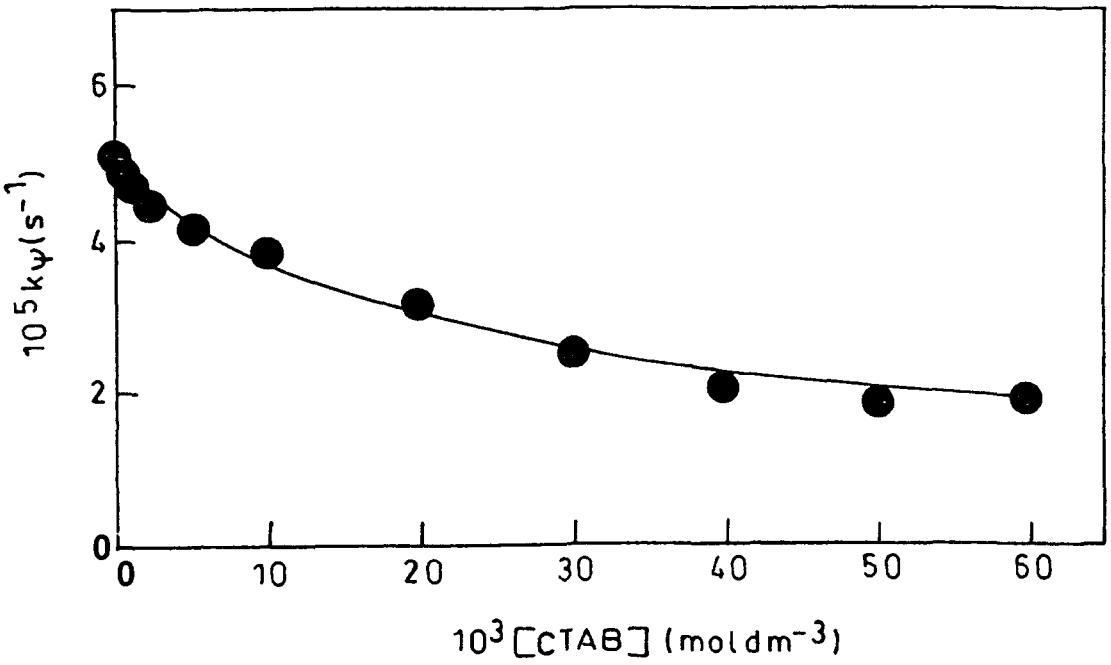


Figure 3.8 Effect of variation of [CTAB] on the values of rate constant (k_ψ).

Reaction Conditions: [Fenuron] = 5.0×10^{-5} mol dm^{-3} and [HCl] =0.1 mol dm^{-3} at 80°C.

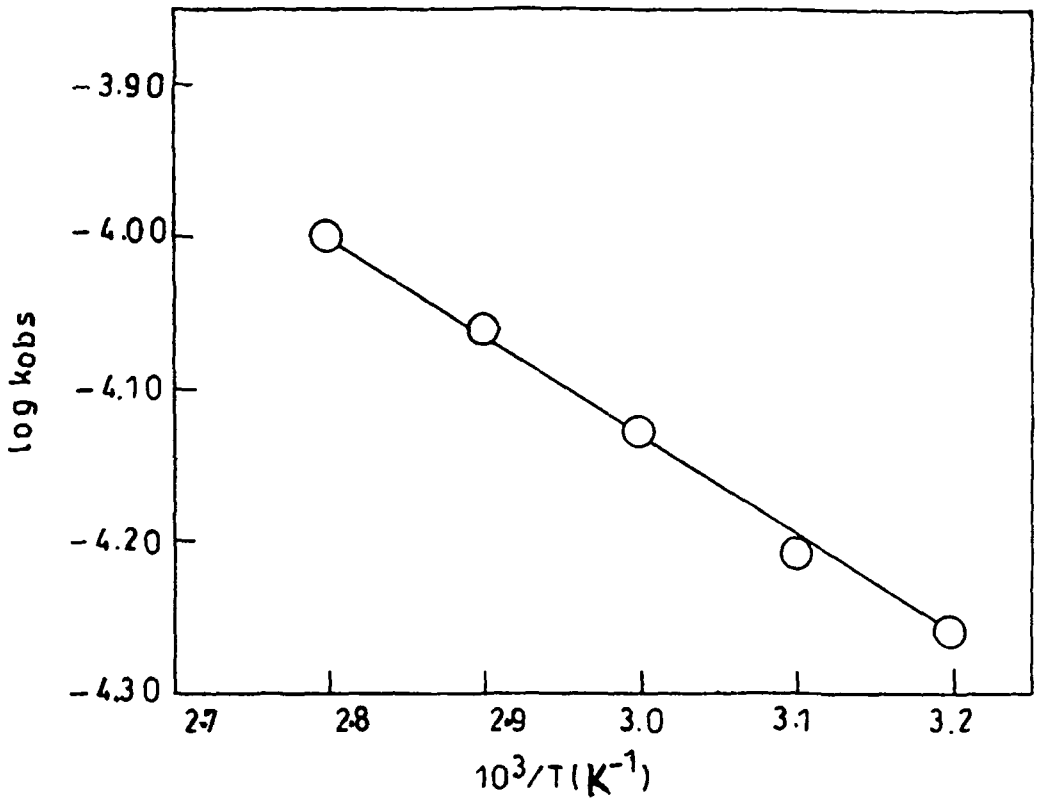


Figure 3.9 Arrhenius plot for acidic hydrolysis of isoproturon in aqueous medium.

Reaction Conditions: [Isoproturon] = 5.0×10^{-5} mol dm^{-3} and [HCl] =0.1 mol dm^{-3}.

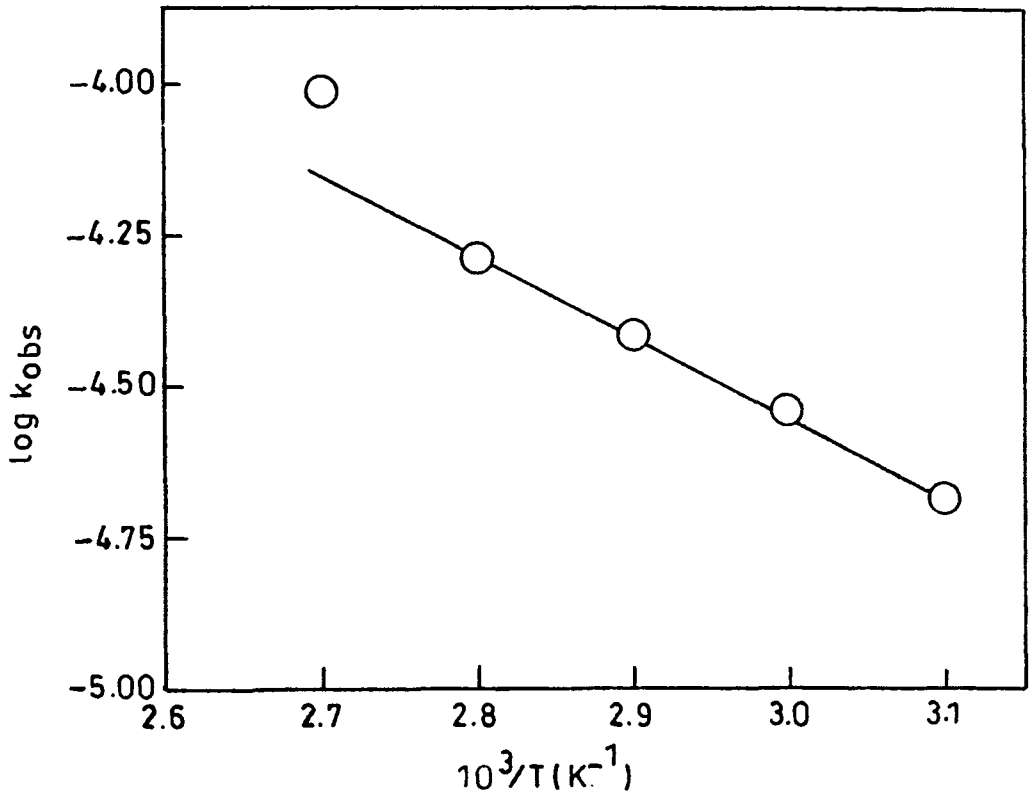


Figure 3.10 Arrhenius plot for acidic hydrolysis of fenuron in aqueous medium.

Reaction Conditions: [Fenuron] = 5.0×10^{-5} mol dm^{-3} and [HCl] =0.1 mol dm^{-3}.

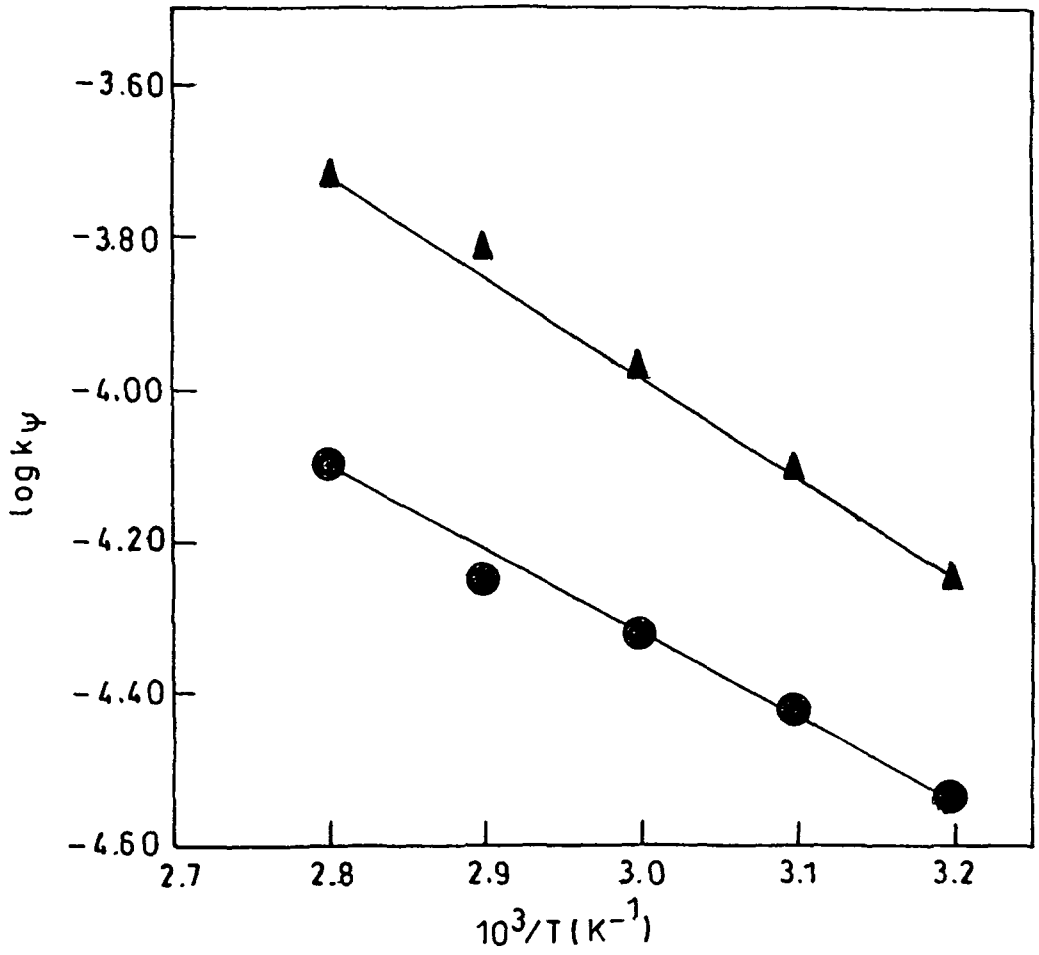


Figure 3.11 Arrhenius plot for acidic hydrolysis of isoproturon in (•) CTAB and (▲) NaLS micelles.

Reaction Conditions: [Isoproturon] = 5.0×10^{-5} mol dm^{-3}; [HCl] =0.1 mol dm^{-3}; [CTAB] =2.0×10^{-2} mol dm^{-3} and [NaLS] =2.0×10^{-2} mol dm^{-3}.

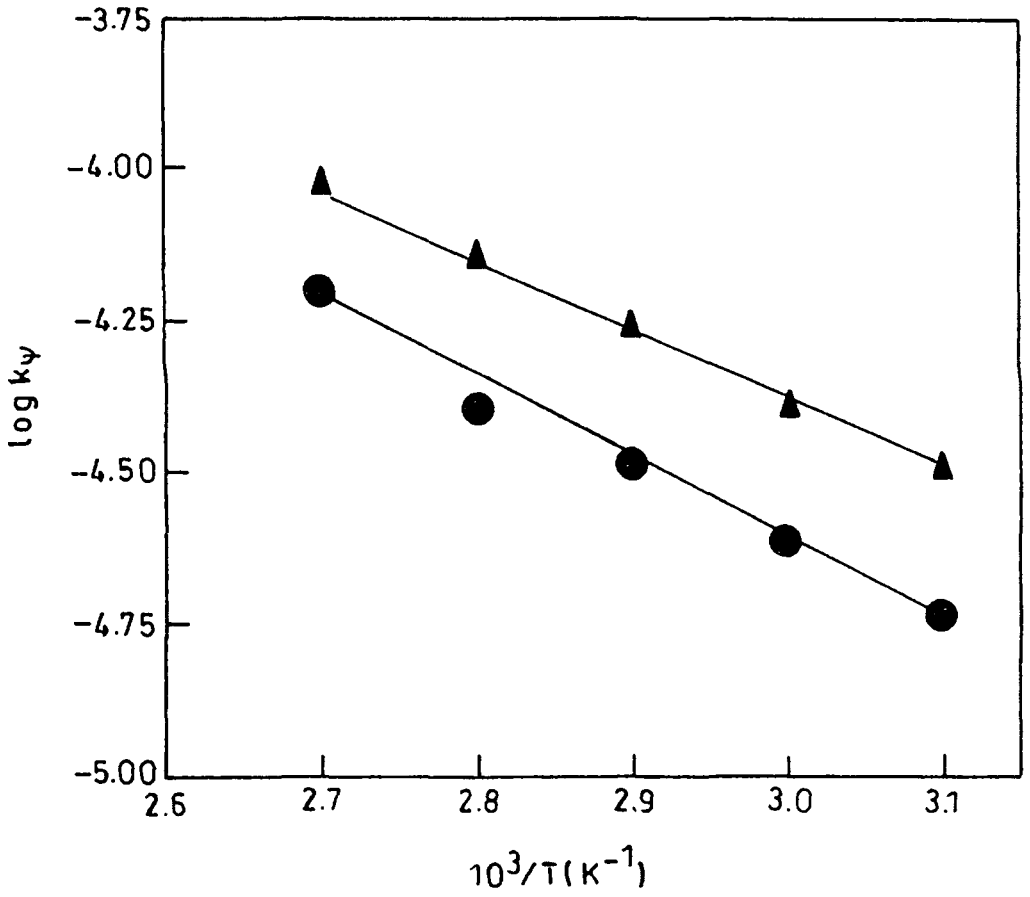


Figure 3.12 Arrhenius plot for acidic hydrolysis of fenuron in (•) CTAB and (▲) NaLS micelles.

Reaction Conditions: [Fenuron] = 5.0×10^{-5} mol dm^{-3}; [HCl] = 0.1 mol dm^{-3}; [CTAB] =1.0×10^{-2} mol dm^{-3} and [NaLS] =1.0×10^{-2} mol dm^{-3}.

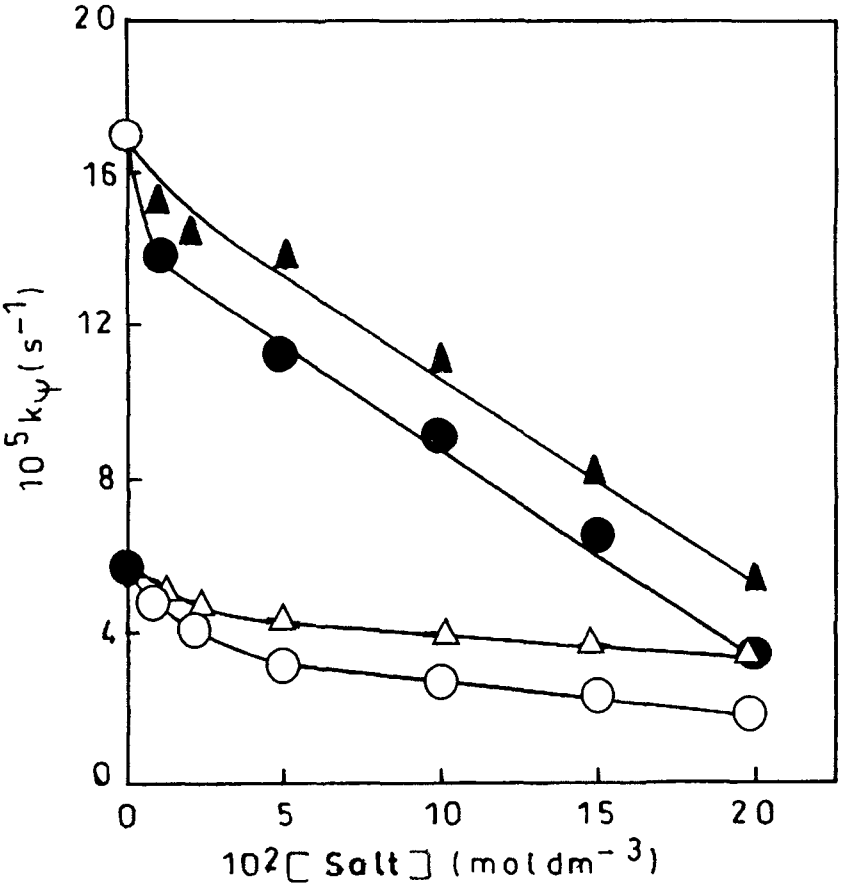


Figure 3.13 Effect of variation of [NaCl] and [KNO_3] on the values of rate constant, k_ψ (▲, •) for KNO_3 and NaCl respectively for [NaLS] and (Δ, o) for KNO_3 and NaCl respectively for [CTAB].

Reaction Conditions: [Isoproturon] = 5.0×10^{-5} mol dm^{-3}; [HCl] =0.1 mol dm^{-3}; [CTAB] =2.0×10^{-2} mol dm^{-3} and [NaLS] =2.0×10^{-2} mol dm^{-3} at 70°C.

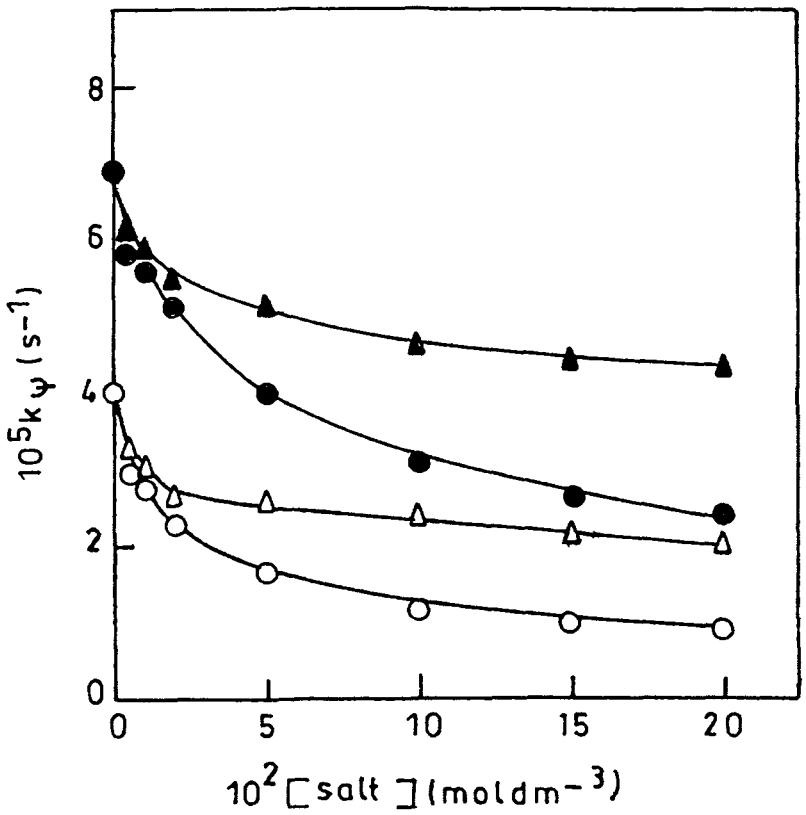


Figure 3.14 Effect of variation of [NaCl] and [KNO_3] on the values of rate constant, k_ψ (▲, •) for KNO_3 and NaCl respectively for [NaLS] and (Δ, o) for KNO_3 and NaCl respectively for [CTAB].

Reaction Conditions: [Fenuron] = 5.0×10^{-5} mol dm^{-3}; [HCl] =0.1 mol dm^{-3}; [CTAB] =1.0×10^{-2} mol dm^{-3} and [NaLS] =1.0×10^{-2} mol dm^{-3} at 80°C.

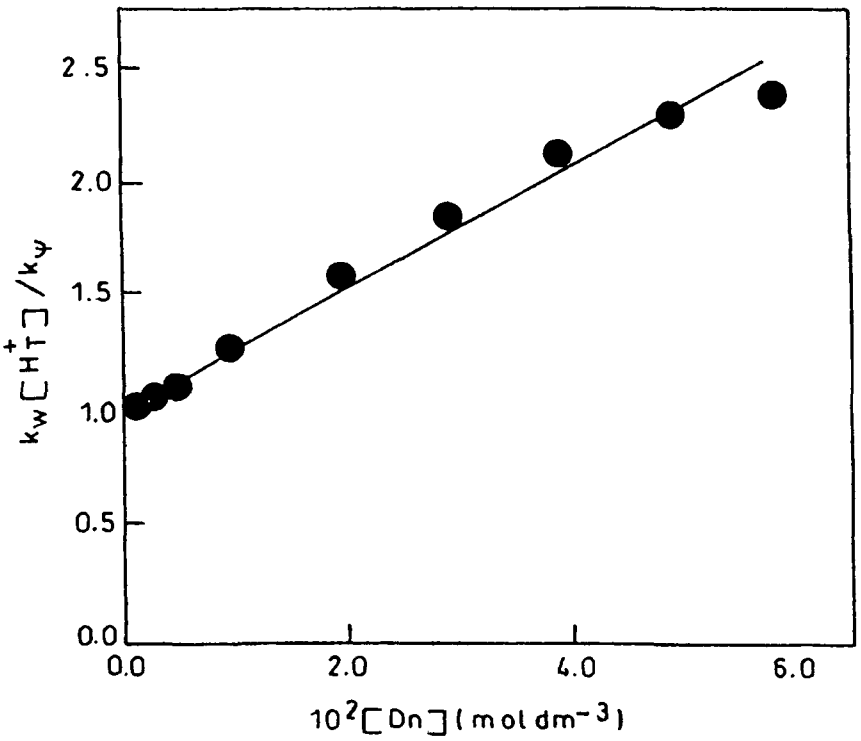


Figure 3.15 Plot of $\frac{k_w[H_T^+]}{k_\psi}$ versus $[D_n]$

Reaction Conditions: [Isoproturon] = 5.0×10^{-5} mol dm^{-3} and [HCl] = 0.1 mol dm^{-3} at 70°C.

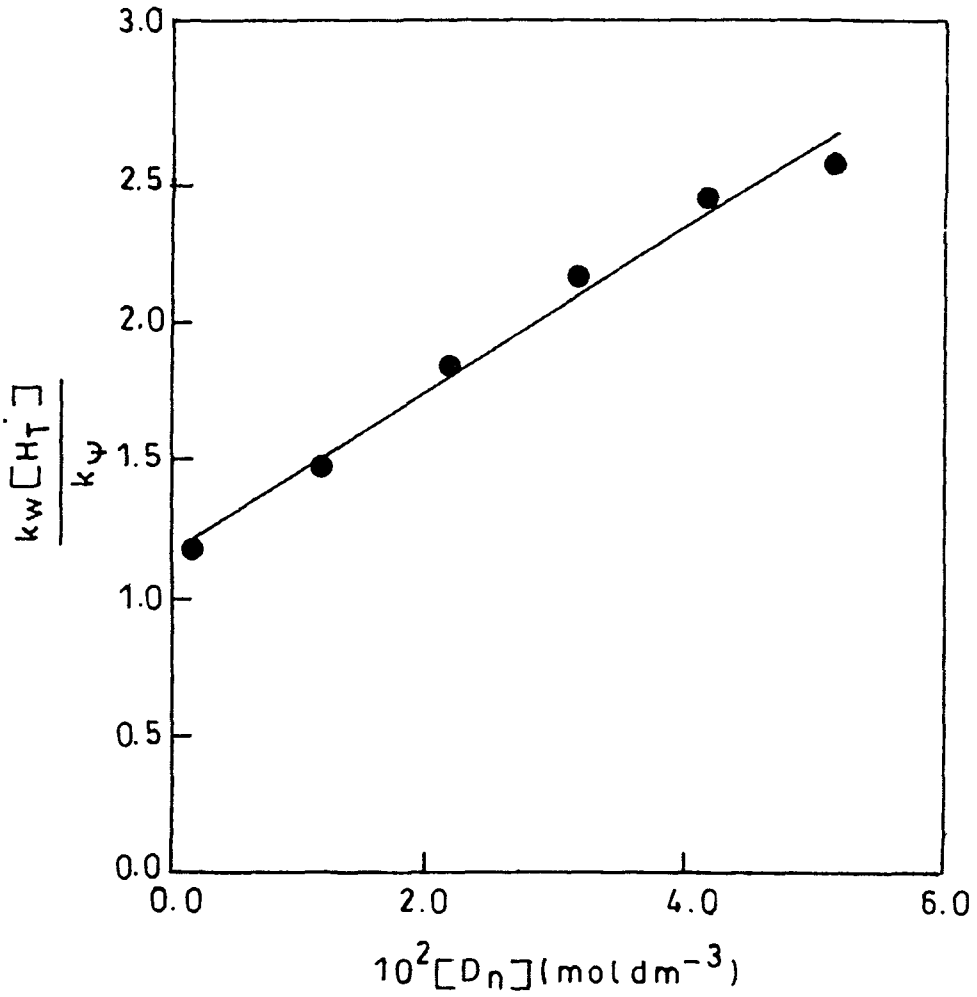


Figure 3.16 Plot of $\frac{k_w[H_T^+]}{k_\psi}$ versus $[D_n]$

Reaction Conditions: [Fenuron] = 5.0×10^{-5} mol dm^{-3} and [HCl] = 0.1 mol dm^{-3} at 80°C.

Chapter-4

Kinetics of Alkaline Hydrolysis of Phenylureas in *CTAB* and *NaLS* Micelles

4.1 Results

4.1.1 Dependence of the Reaction Rate on [Phenylurea]

The rate constants for alkaline hydrolytic reaction of phenylurea (isoproturon and fenuron) were obtained by carrying out experiments at different initial concentrations of phenylurea in the range from 4.0×10^{-5} mol dm^{-3} to 10×10^{-5} mol dm^{-3}. The concentration of sodium hydroxide was kept constant at 0.1 mol dm^{-3}at temperatures 70°C and 80°C for isoproturon and fenuron, respectively. The pseudo-first order rate constants (k_{obs}) were calculated by using computer program and are given in Tables 4.1-4.2.

To study the dependence of the order of reaction on [phenylurea] in the presence of NaLS and CTAB micelles, the kinetic studies were carried out in the presence of these surfactants. The concentrations of CTAB and NaLS for isoproturon were 2.0×10^{-2} mol dm^{-3} and for fenuron were 1.0×10^{-2} mol dm^{-3}. The results are given in Tables 4.1-4.2 and are in Figures 4.1-4.2. It was observed that the values of rate constant were independent of the initial concentrations of isoproturon and fenuron. Thus, the order of reaction with respect to [phenylurea] is unity in both aqueous and micellar media.

4.1.2 Dependence of the Reaction Rate on [Sodium Hydroxide]

The order of the reaction with respect to sodium hydroxide concentration was determined by carrying out the kinetic experiments at various concentrations of sodium hydroxide in the range from 1.0×10^{-2} to 1.0 mol dm^{-3}. The concentration of

phenylurea was kept constant at 5.0×10^{-5} mol dm^{-3} at fixed temperature 70°C and 80°C for isoproturon and fenuron respectively. The studies in the presence of surfactant were carried out at [NaLS] and [CTAB] (=2.0×10^{-2} mol dm^{-3} for isoproturon) and [NaLS] and [CTAB] (= 1.0×10^{-2} mol dm^{-3} for fenuron). The remaining conditions of temperature and concentration of reactants were the same as those for aqueous medium. The results are presented in Tables 4.3-4.4 and depicted graphically in Figures 4.3 – 4.4.

4.1.3 Dependence of the Reaction Rate on [Sodium Lauryl Sulfate]

To study the influence of NaLS micelles on the pseudo first-order reaction rate, a series of kinetic runs were performed at different [NaLS] (=5.0×10^{-4} mol dm^{-3} – 5.0×10^{-2} mol dm^{-3}) with fixed concentrations of phenylurea (= 5.0×10^{-5} mol dm^{-3}) and NaOH (=0.1 mol dm^{-3}). The k_ψ values decreased continuously with increasing [NaLS] and finally reached to an almost constant value. The results are given in Tables 4.5 – 4.6 and in Figures 4.5-4.6.

4.1.4 Dependence of the Reaction Rate on [Cetyltrimethyl-ammonium Bromide]

The pseudo first-order rate constant (k_ψ) dependence on CTAB concentration was investigated by carrying out a series of kinetic runs at different [CTAB] in the range from 5.0×10^{-4} mol dm^{-3} to 5.0×10^{-2} mol dm^{-3} with fixed concentrations of phenylurea (= 5.0×10^{-5} mol dm^{-3}) and NaOH (=0.1 mol dm^{-3}) at 70°C (for isoproturon) and 80°C (for fenuron) temperatures.

The variation of k_ψ values shows typical behaviour. It increases with increasing [CTAB], to reach a maximum value and then decreases with further increase in [CTAB]. These results are summarized in Tables 4.7-4.8 and in Figures 4.7-4.8.

4.1.5 Dependence of the Reaction Rate on Temperature

Kinetic experiments were carried out at different temperatures (40°C-90°C) keeping the concentrations of phenylurea (=5.0×10^{-5} mol dm^{-3}) and NaOH (=0.1 mol dm^{-3}) constant. In presence of micelles the effect of temperature on the rate of alkaline hydrolytic reaction of phenylurea was studied at [NaLS] (= 2.0×10^{-2} mol dm^{-3} for isoproturon and 1.0×10^{-2} mol dm^{-3} for fenuron) and [CTAB] (= 2.0×10^{-2} mol dm^{-3} for isoproturon and 1.0×10^{-2} mol dm^{-3} for fenuron). The rate constants calculated at different temperatures are given in Tables 4.9- 4.10. The plots of log k_{obs} versus $\frac{1}{T}$ are shown in Figures 4.9–4.10. The plots of log k_ψ versus $\frac{1}{T}$ for alkaline hydrolysis of phenylurea in CTAB and NaLS micelles are shown in Figures 4.11–4.12.

The kinetic parameters, e.g., energy of activation, E_a, standard entropy change, $-\Delta S^{\#}$ and standard enthalpy change, $\Delta H^{\#}$ were determined from the plot of k_{obs} versus $\frac{1}{T}$ and are given in Tables 4.9- 4.10.

4.1.6 Dependence of the Reaction Rate on [Salt]

The effect of salts on the alkaline hydrolytic reaction of phenylurea in presence and absence of NaLS and CTAB

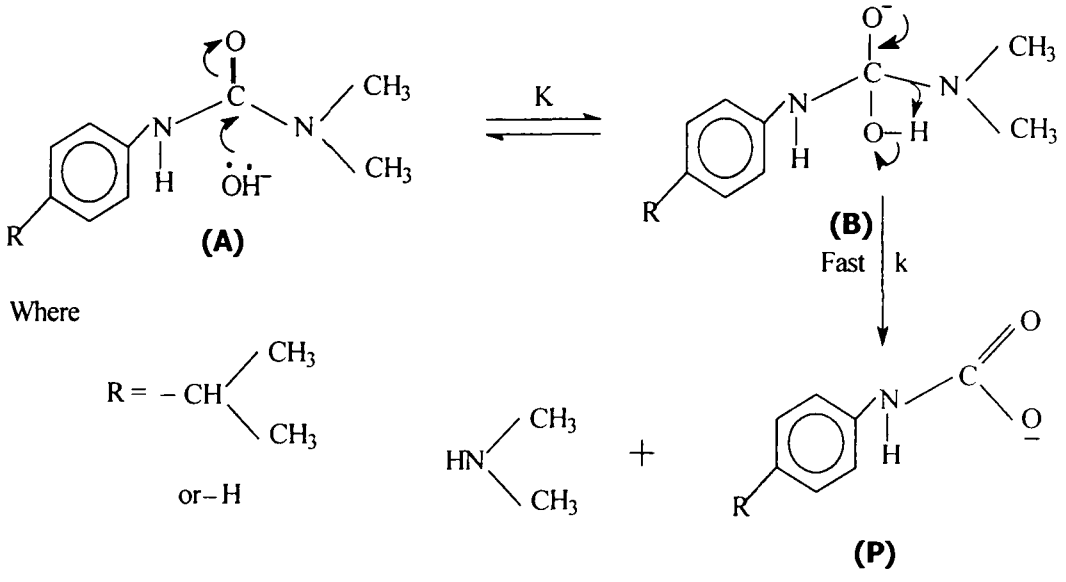
surfactants were carried out at fixed concentrations of phenylurea (=5.0× 10^{-5} mol dm^{-3}), NaOH (=0.1 mol dm^{-3}), and surfactants (=2.0 × 10^{-2} mol dm^{-3} for isoproturon and 1.0 ×10^{-2} mol dm^{-3} for fenuron). The values of rate constant were found to be independent of [salt] in aqueous solution but the values of rate constant decreased with the increasing salt concentrations in micellar media. The results are summarized in Tables 4.11- 4.12 and are presented in Figures 4.13-4.14.

4.2 Discussion

4.2.1 Reaction in Aqueous Medium

The hydrolytic reaction of phenylureas (isoproturon and fenuron) followed first-order kinetics in [phenylurea] and fractional order in [NaOH] as observed from the kinetic data presented in Tables 4.1-4.4 and Figures 4.1-4.4.

At lower OH^- concentration, the hydrolysis of phenylureas is presumed to occur through the attack of OH^- to the corbonyl carbon. As a result, formation of an intermediate hydroxide ion addition complex takes place. Water acting as general acid attacks on this addition complex and facilitates the elimination of dimethylamine.[119] This leads to the formation of corresponding carbamate (Scheme 4.1)



Scheme 4.1

This reaction follows an elimination mechanism and the rate determining step is the attack of water molecule leading to the formation of phenyl carbamate. This carbamate is stable[138,140] in basic and neutral solutions, but in acidic solution it is very unstable and decomposes rapidly to form corresponding aniline and carbon dioxide.[141]

The observed rate of hydrolysis can be given by

$$v = k_{obs}[\text{phenylurea}]_T \qquad (4.1)$$

corresponding to the scheme 4.1, the rate equation is given by

$$\text{rate} = \frac{dp}{dt} = k[B] \qquad (4.2)$$

$$= kK[OH^-][A] \qquad (4.3)$$

The total phenylurea concentration is given by :

$$[A]_T = [A] + [B]$$

$$= [A] + k[OH^-][A]$$

$$= [A](1 + K[OH^-])$$

or $$[A] = \frac{[A]_T}{1 + K[OH^-]}$$

On putting the value of [A] in terms of total phenylurea concentrations, the equation (4.3) becomes:

$$\frac{dp}{dt} = \frac{kK[OH^-][A]_T}{1 + K[OH^-]} \qquad (4.4)$$

On comparing equations 4.1 and 4.4, we get

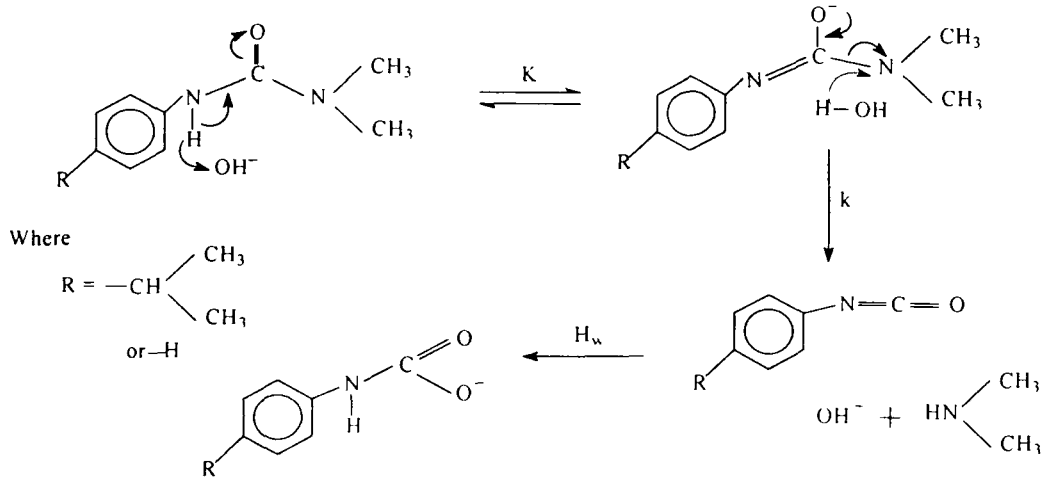
$$k_{obs} = \frac{kK[OH^-]_T}{1+K[OH^-]} \qquad (4.5)$$

On inverting equation (4.5), we obtained

$$\frac{1}{k_{obs}} = \frac{1}{k} + \frac{1}{kK[OH^-]}$$

Thus a plot of $\frac{1}{k_{obs}}$ versus $\frac{1}{[NaOH]}$ should give a straight line and our observed results on varying $[OH^-]$ (Figures 4.17-4.18) support the mechanism presented in Scheme 4.1.

At high OH^- concentrations the hydrolysis of phenylurea proceeds through the fast reversible deprotonation of amino-nitrogen (attached to phenyl group) followed by slow protonation of dimethyl amino nitrogen by water.[120] The reaction may be represented by the following Scheme 4.2.



Scheme 4.2

During hydrolysis of phenylurea at high pH, the intermediate, phenyl isocyanate hydrolyze rapidly to yield phenyl carbamate. Moodie and Coworkers[124] reported a half life value of 20s for hydrolysis of phenyl isocyanate in aqueous solution at

25°C. Thus under our reaction conditions of $[OH^-]$ (= 0.1 mol dm^{-3}), it can be safely concluded that the reaction occurs via deprotonation of nitrogen leading to the formation of unstable intermediate phenyl isocyanate and finally phenyl carbamate. The levelling behaviour on the rate of hydrolytic reaction by $[OH^-]$ may be attributed to the rate determining attack of H_2O on dimethyl nitrogen. At pH higher than 10, the carbamate is relatively long lived. In the acidic and neutral media the carbamate decarboxylate rapidly to yield aniline.[143] With the increase in basicity the activity of water (which act as general acid) decrease and, therefore, the rate of hydrolysis become constant.

4.2.2 Reaction in Micellar Media

The rate of hydrolysis of phenylurea studied in alkaline medium in the presence of cationic, CTAB micelles showed a sigmoidal behaviour, in which the maximum for isoproturon was observed at [CTAB] (=2.0 × 10^{-2} mol dm^{-3}) and for fenuron at [CTAB] (= 1.0 ×10^{-2} mol dm^{-3}). The further increase in [CTAB] decreased the rate constant values as shown in Figures 4.7-4.8. The observed higher rate in CTAB could be attributed to the binding of both phenylurea and OH^- to the positively charged micellar surface. The electron rich carbonyl part of phenylurea is oriented towards the positively charged surface layer of CTAB micelles and the non-polar part i.e., phenyl group is immersed towards the micellar core. Thus, the reactive group of phenylurea and OH^- lie in the Stern's layer of the same micelle of CTAB. Therefore, reaction catalyzed by CTAB micelles, occurs mainly

in the Stern's layer region. With the increase in [CTAB] the local molarities of phenylurea and OH^- ions in the Stern's layer are increased and therefore, the enhancement in the rate of reaction is observed.

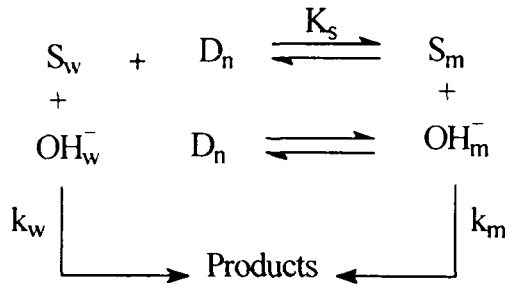
Two distinct effects can be considered for decrease in rate of hydrolysis at higher CTAB concentrations. Firstly, as the concentration of CTAB increases, the number of the unreactive Br^- ions also increases and replaces micellar bound OH^- ions. The displacement of OH^- from the vicinity of Stern's layer causes decrease in $[OH^-]$ in the micellar pseudophase. Secondly, the increase in CTAB concentration results into the formation of increased number of micelles and causes in the dilution of micellar bound $[OH^-]$. Thus in both the cases, the OH^- concentration in the micellar pseudophase is decreased. It results in the dilution of OH^- in the micellar pseudophase and therefore, reduces the rate of reaction.

The reaction in the presence of CTAB micelles too followed pseudo first-order with respect to [phenylurea] and fractional order in $[OH^-]$ as evident from the data presented in Tables 4.7-4.8 and Figures 4.7-4.8. Thus, the observed data suggest that the reaction mechanism remains the same both in presence of CTAB micelles and in aqueous medium with all possible intermediary situations. A straight line plot for $\frac{1}{k_\psi}$ versus $\frac{1}{[NaOH]}$ in the presence of micelles supports that the

reaction followed the same mechanism in aqueous and micellar media (Figures 4.17-4.18).

The quantitative treatment of the increased rate of alkaline hydrolysis of phenylurea upon addition of CTAB micelles can be explained on the basis of pseudophase model of micelles (as has been discussed in chapter 3). In this model the electrostatic and hydrophilic interactions have been considered. The rate of alkaline hydrolysis of phenylurea is affected by the ionic micelles and the reactions under discussion follow this general pattern. The electrostatic and hydrophobic interactions between micelles and reactants transition states and products are involved in the micellar solutions. The micellar surface can attract or repel ionic species due to electrostatic interactions where as hydrophobic interaction can bring about incorporation into micelles. In alkaline medium phenylurea is deprotonated and this negatively charged phenylurea get more strongly bonded to cationic, CTAB micelles. Thus the micelles faciliate the extensive build up of deprotonated phenylureas in the region of Stern's layer.

Although, several kinetic equations based on the general Scheme 4.3 have been developed, the most successful appears to be that of Bunton who suggested expression (4.6). It takes into account the solubilization of both the reactants into the micellar pseudophase.



Scheme 4.3

On the basis of Scheme 4.3, the first-order rate equation can be transformed in terms of second-order rate equation (4.6).

$$k_\psi = \frac{k_w [OH_T^-] + (k_m K_S - k_w) m_{OH^-} [D_n]}{1 + K_S [D_n]} \qquad (4.6)$$

The terms used in this equation have their usual meaning as described in chapter 3.

For the reactive OH^- and Br^- as micelles counter ion, the ion exchange equilibrium can be expressed as [142]

$$OH_w^- + Br_m^- \overset{K_{OH^-/Br^-}}{\rightleftharpoons} OH_m^- + Br_w^- \qquad (4.7)$$

$$\text{and } K_{OH^-/Br^-} = \frac{[OH_m^-][Br_w^-]}{[OH_w^-][Br_m^-]} \qquad (4.8)$$

$$m_{OH} = [OH_m] / [D_n]$$

m_{OH^-} in term of K_{OH^-/Br^-} is expressed by the following quadratic equation:

$$m_{OH}^2 + m_{OH} \left[\frac{[OH_T^-] + K_{OH/Br} [Br_T^-]}{(K_{OH/Br} - 1)[Dn]} - \beta \right] - \frac{\beta [OH_T^-]}{(K_{OH/Br} - 1)[D_n]} = 0 \qquad (4.9)$$

where β is the fraction of neutralized micellar surface (for CTAB β = 0.80)[25].

The fitting values of k_m, $K_{OH^-/Br}$ and K_S were obtained from the computer program by minimizing the deviation between the simulation and the observed values for k_ψ – [surfactant] profile. The values of these parameters are given in Tables 4.13-4.14.

The cationic micelles of CTAB are effective in incorporating phenylurea in alkaline medium as it is evident from the large values of K_S for isoproturon and fenuron as given Tables 4.13-4.14. Interestingly, on the other hand, the value of K_S is lower in case of acidic hydrolysis of phenylureas (for isoproturon and fenuron) in comparison to alkaline hydrolysis of phenylureas. This indicates that hydrophobicity of the phenylureas molecule is diminished in presence of OH^- with CTAB and electrostatic interaction become were pronounced. It is well established that the addition of anions of unreactive electrolyte in solution of cationic, CTAB surfactant affects the system in many ways.

An attempt was made to see the effect of anionic NaLS micelles on the alkaline hydrolysis of phenylureas at constant [phenylurea] (= 5.0×10^{-5} mol dm^{-3}) in 0.1 M NaOH. A continuous decrease in k_ψ was observed with increase in NaLS concentration. The inhibition of the reaction is explained by considering the fact that OH^- being anionic, does not bind to the NaLS micelles in Stern's layer and exists in aqueous medium.

The deprotonated phenylureas or negatively charged tetrahedral intermediate is also being repelled by the negatively charged head group of NaLS micelles. Thus, the reaction in the presence of NaLS micelles occur mainly in aqueous pseudophase and the terms k_m and m_{OH} are considered to be zero in equation 4.6. The equation (4.6) is now reduced to :

$$k_\psi = \frac{k_\psi [OH_T^-]}{1 + K_S [D_n]}$$

$$\text{or} \quad \frac{k_w [OH_T^-]}{k_\psi} = 1 + K_S [D_n] \qquad (4.10)$$

Therefore, from equation 4.10 a straight line plot should be obtained for $\frac{k_w [OH_T^-]}{k_\psi}$ versus $[D_n]$. Figures 3.15-3.16 demonstrate the validity of relationship given in equation 4.10. The values of the binding constants of phenylureas with NaLS micelles are given in Tables 4.13 - 4.14. The low values of K_S indicate weak association between anionic NaLS micelles and phenlyureas. The binding of phenylureas with NaLS micelles may be due to their hydrophobicity or binding as co-ions.

The effect of temperature on the rate constant for the alkaline hydrolysis of phenylureas with sodium hydroxide in presence of surfactants was used to evaluate activation parameters. The activation parameters were calculated by least square method. The enthalpy and entropy of activation were calculated by using Eyring relationship and are presented in Tables 4.6 - 4.7.

The decrease in entropy of the reaction in presence of micelles suggests that reactants are in greater degree of orderliness while an increase in entropy shows greater degree of randomness. The interaction with micelles favour the charge dispersion of reactants in the transition state and its greater degree of orderliness results in the increase in the values of rate constants.

Figures 4.13 - 4.14 show the inhibition effect of added salts (KNO_3 and NaCl) on the alkaline hydrolytic reaction of phenylureas. Rate inhibition in micellar media by added salt or electrolyte can be considered to be due to the change in shape and size of micelles and/ or exclusion of reactants from the micellar pseudophase. The addition of NaCl decreased the rate of reaction while addition of KNO_3 had less inhibiting effect.

Inhibition by the addition of salts also could be due to competitive binding of counter ions present with micelles.[133,134] The addition of salt decreases the concentration of OH^- in the Stern's layer and thereby decrease the rate. Since [CTAB] in presence of high salt concentration would be sufficiently shielded from its electrostatic effect by the ionic atmosphere, its micelles, in these media would behave like a non ionic micelles, inspite of their different micellar surface environment. The inhibition by the added salt may also be due to increase in the aggregation number thereby causing to decrease as the number of micelles.

Table. 4.1

Effect of variation of [Isoproturon] on rate constants in the aqueous (k_{obs}) and in presence of CTAB and NaLS micelles (k_{ψ}) for alkaline hydrolytic reaction of isoproturon.

Reaction conditions:

[Isoproturon] = 5.0×10^{-5} mol dm^{-3}

[NaOH] = 0.1 mol dm^{-3}

Temperature = 70°C

10^5 [Isoproturon] (mol dm^{-3})	Rate Constants		
	Aqueous $10^5 k_{obs}$ (s^{-1})	CTAB $10^5 k_{\psi}$ (s^{-1})	NaLS $10^5 k_{\psi}$ (s^{-1})
4.0	4.26±0.12	6.49±0.18	3.14±0.13
5.0	4.45±0.15	6.63±0.21	3.26±0.12
6.0	4.82±0.13	6.73±0.25	3.32±0.14
8.0	5.02±0.21	6.82±0.22	3.39±0.13
10.0	5.12±0.19	6.93±0.20	3.45±0.15

[CTAB] = 2.0×10^{-2} mol dm^{-3}

[NaLS] = 2.0×10^{-2} mol dm^{-3}

Table. 4.2

Effect of variation of [Fenuron] on rate constants in the aqueous (k_{obs}) and in presence of CTAB and NaLS micelles (k_{ψ}) for alkaline hydrolytic reaction of fenuron.

Reaction conditions:

[Fenuron] = 5.0×10^{-5} mol dm^{-3}

[NaOH] = 0.1 mol dm^{-3}

Temperature = 80°C

10^5 [Fenuron] (mol dm^{-3})	Rate Constants		
	Aqueous $10^5 k_{obs}$ (s^{-1})	CTAB $10^5 k_{\psi}$ (s^{-1})	NaLS $10^5 k_{\psi}$ (s^{-1})
4.0	5.06±0.23	7.83±0.22	3.61±0.11
5.0	5.18±0.20	7.97±0.25	3.74±0.12
6.0	5.23±0.21	8.01±0.28	3.82±0.16
8.0	5.29±0.22	8.06±0.29	3.97±0.16
10.0	5.39±0.17	8.12±0.23	4.04±0.19

[CTAB] = 1.0×10^{-2} mol dm^{-3}

[NaLS] = 1.0×10^{-2} mol dm^{-3}

Table. 4.3

Effect of variation of [NaOH] on rate constants in the aqueous (k_{obs}) and in presence of CTAB and NaLS micelles (k_{ψ}) for the alkaline hydrolytic reaction of isoproturon.

Reaction conditions:

[Isoproturon] = 5.0×10^{-5} mol dm^{-3}

Temperature = 70°C

[NaOH] (mol dm^{-3})	Rate Constants		
	Aqueous $10^5 k_{obs}$ (s^{-1})	CTAB $10^5 k_{\psi}$ (s^{-1})	NaLS $10^5 k_{\psi}$ (s^{-1})
0.01	1.21±0.04	1.44±0.05	1.14±0.04
0.05	3.21±0.09	3.71±0.10	2.74±0.07
0.1	4.47±0.16	6.63±0.21	3.29±0.13
0.2	5.08±0.15	6.88±0.22	4.01±0.12
0.3	5.46±0.20	7.11±0.27	4.48±0.15
0.5	5.64±0.18	7.38±0.29	4.62±0.18
0.8	5.70±0.19	7.50±0.23	4.70±0.17
1.0	5.77±0.22	7.59±0.26	4.74±0.11

[CTAB] = 2.0×10^{-2} mol dm^{-3}

[NaLS] = 2.0×10^{-2} mol dm^{-3}

Table. 4.4

Effect of variation of [NaOH] on rate constants in the aqueous (k_{obs}) and in presence of CTAB and NaLS micelles (k_ψ) for the alkaline hydrolytic reaction of fenuron.

Reaction conditions:

[Fenuron] = 5.0×10^{-5} mol dm^{-3}

Temperature = 80°C

[NaOH] (mol dm^{-3})	Rate Constants		
	Aqueous $10^5 k_{obs}$ (s^{-1})	CTAB $10^5 k_\psi$ (s^{-1})	NaLS $10^5 k_\psi$ (s^{-1})
0.01	2.56±0.07	3.49±0.10	2.06±0.06
0.02	3.61±0.11	4.67±0.14	2.98±0.10
0.05	4.81±0.18	6.31±0.19	3.24±0.12
0.1	5.18±0.20	7.97±0.25	3.74±0.12
0.2	5.41±0.22	8.40±0.26	4.09±0.19
0.3	5.62±0.16	8.77±0.28	4.42±0.14
0.5	5.81±0.18	8.94±0.31	4.61±0.21
0.8	5.89±0.21	9.06±0.29	4.69±0.20
1.0	5.93±0.23	9.12±0.37	4.74±0.17

[CTAB] = 1.0×10^{-2} mol dm^{-3}

[NaLS] = 1.0×10^{-2} mol dm^{-3}

Table. 4.5

Effect of variation of [NaLS] on rate constants (k_ψ) for the alkaline hydrolytic reaction of isoproturon.

Reaction conditions:

[Isoproturon] = 5.0×10^{-5} mol dm^{-3}

[NaOH] = 0.1 mol dm^{-3}

Temperature = 70°C

10^3 [NaLS] (mol dm^{-3})	Rate Constants
	$10^5 k_\psi$ (s^{-1})
0.0	4.47±0.16
0.5	4.40±0.14
1.0	4.01±0.12
2.0	3.71±0.14
5.0	3.53±0.13
10.0	3.46±0.15
15.0	3.35±0.14
20.0	3.26±0.08
25.0	3.23±0.11
30.0	3.20±0.10
40.0	3.16±0.09
50.0	3.10±0.12

Table. 4.6

Effect of variation of [NaLS] on rate constants (k_ψ) for the alkaline hydrolytic reaction of fenuron.

Reaction conditions:

[Fenuron] = 5.0×10^{-5} mol dm^{-3}

[NaOH] = 0.1 mol dm^{-3}

Temperature = 80°C

10^3 [NaLS] (mol dm^{-3})	Rate Constants $10^5 k_\psi$ (s^{-1})
0.0	5.18±0.20
0.5	5.01±0.19
1.0	4.83±0.14
2.0	4.42±0.15
5.0	3.98±0.13
10.0	3.74±0.13
15.0	3.32±0.11
20.0	3.14±0.10
30.0	2.93±0.12
40.0	2.84±0.15
50.0	2.80±0.14

Table. 4.7

Effect of variation of [CTAB] on rate constants (k_ψ) for the alkaline hydrolytic reaction of isoproturon.

Reaction conditions:

[Isoproturon] = 5.0×10^{-5} mol dm^{-3}

[NaOH] = 0.1 mol dm^{-3}

Temperature = 70°C

10^3 [CTAB] (mol dm^{-3})	Rate Constants $10^5 k_\psi$ (s^{-1})
0.0	4.47±0.16
0.5	4.48±0.13
1.0	4.61±0.18
2.0	4.87±0.16
5.0	5.52±0.21
10.0	6.63±0.23
15.0	6.67±0.20
20.0	6.74±0.19
25.0	5.84±0.22
30.0	3.89±0.14
40.0	3.39±0.12
50.0	3.22±0.10

Table. 4.8

Effect of variation of [CTAB] on rate constants (k_ψ) for the alkaline hydrolytic reaction of fenuron.

Reaction conditions:

[Fenuron] = 5.0×10^{-5} mol dm^{-3}

[NaOH] = 0.1 mol dm^{-3}

Temperature = 80°C

10^3 [CTAB] (mol dm^{-3})	Rate Constants
	$10^5 k_\psi$ (s^{-1})
0.0	5.18±0.20
0.5	5.37±0.17
1.0	5.97±0.23
2.0	6.73±0.21
5.0	7.39±0.28
10.0	7.97±0.31
15.0	6.81±0.22
20.0	4.93±0.14
30.0	3.64±0.11
40.0	3.02±0.10
50.0	2.84±0.08

Table. 4.9

Effect of variation of temperature on rate constants in the aqueous (k_{obs}) and in presence of CTAB and NaLS micelles (k_{ψ}) for the alkaline hydrolytic reaction of isoproturon.

Reaction conditions:

[Isoproturon] = 5.0×10^{-5} mol dm^{-3}

[NaOH] = 0.1 mol dm^{-3}

Temperature (°C)	Rate Constants		
	Aqueous $10^5 k_{obs}$ (s^{-1})	CTAB $10^5 k_{\psi}$ (s^{-1})	NaLS $10^5 k_{\psi}$ (s^{-1})
40	1.31±0.05	1.68±0.08	1.64±0.07
50	2.70±0.09	2.88±0.11	2.07±0.08
60	3.81±0.11	3.98±0.12	2.77±0.10
70	4.47±0.16	6.62±0.20	3.26±0.13
80	6.84±0.22	8.08±0.30	5.11±0.15
Activation Parameters			
E_a (kJ mol^{-1})	35.31±1.23	39.01±1.56	24.95±0.91
$\Delta H^{\#}$ (kJ mol^{-1})	32.83±1.02	36.53±1.43	22.47±0.82
$-\Delta S^{\#}$ (JK^{-1} mol^{-1})	233.53±4.68	219.56±4.41	266.45±5.01

[CTAB] = 2.0×10^{-2} mol dm^{-3}

[NaLS] = 2.0×10^{-2} mol dm^{-3}

Table. 4.10

Effect of variation of temperature on rate constants in the aqueous (k_{obs}) and in presence of CTAB and NaLS micelles (k_{ψ}) for the alkaline hydrolytic reaction of fenuron.

Reaction conditions:

[Fenuron] = 5.0×10^{-5} mol dm^{-3}

[NaOH] = 0.1 mol dm^{-3}

Temperature (°C)	Rate Constants		
	Aqueous $10^5 k_{obs}$ (s^{-1})	CTAB $10^5 k_{\psi}$ (s^{-1})	NaLS $10^5 k_{\psi}$ (s^{-1})
50	1.23±0.05	1.97±0.08	1.14±0.04
60	2.14±0.06	3.11±0.09	1.99±0.07
70	3.39±0.11	4.84±0.13	2.91±0.08
80	5.18±0.19	7.97±0.24	3.74±0.10
90	11.34±0.29	14.76±0.30	7.89±0.20
Activation Parameters			
E_a (kJ mol^{-1})	51.82±1.29	48.33±1.24	43.85±1.19
$\Delta H^{\#}$ (kJ mol^{-1})	49.34±1.43	45.87±1.36	41.34±1.39
$-\Delta S^{\#}$ (JK^{-1} mol^{-1})	223.56±4.01	235.24±4.36	250.41±4.68

[CTAB] = 1.0×10^{-2} mol dm^{-3}

[NaLS] = 1.0×10^{-2} mol dm^{-3}

Table. 4.11

Effect of variation of inorganic salts on rate constants in the presence of CTAB and NaLS micelles (k_ψ) for the alkaline hydrolytic reaction of isoproturon.

Reaction conditions:

[Isoproturon] = 5.0×10^{-5} mol dm^{-3}

[NaOH] = 0.1 mol dm^{-3}

Temperature = 70°C

10^2 [salts] (mol dm^{-3})	Rate Constants $10^5 k_\psi$ (s^{-1})			
	in CTAB		in NaLS	
	NaCl	KCl	NaCl	KCl
0.0	6.63±0.22	6.63±0.22	3.26±0.10	3.26±0.10
0.5	5.94±0.24	6.11±0.15	3.14±0.11	3.21±0.12
1.0	5.54±0.19	5.84±0.13	3.01±0.09	3.14±0.10
2.0	5.02±0.15	5.39±0.15	2.73±0.07	3.09±0.09
5.0	4.22±0.16	4.98±0.11	2.48±0.08	2.94±0.08
10.0	3.04±0.10	4.46±0.10	2.01±0.06	2.83±0.07
15.0	2.78±0.07	4.32±0.12	1.71±0.08	2.66±0.06
20.0	2.52±0.05	4.30±0.14	1.31±0.05	2.54±0.04

[CTAB] = 2.0×10^{-2} mol dm^{-3}

[NaLS] = 2.0×10^{-2} mol dm^{-3}

Table. 4.12

Effect of variation of inorganic salts on rate constants in the presence of CTAB and NaLS micelles (k_ψ) for the alkaline hydrolytic reaction of fenuron.

Reaction conditions:

[Fenuron] = 5.0×10^{-5} mol dm^{-3}

[NaOH] = 0.1 mol dm^{-3}

Temperature = 80°C

10^2 [salts] (mol dm^{-3})	Rate Constants			
	$10^5 k_\psi$ (s^{-1})			
	in CTAB		in NaLS	
	NaCl	KNO_3	NaCl	KNO_3
0.0	7.97±0.22	7.97±0.22	3.74±0.12	3.74±0.12
0.5	6.82±0.18	7.48±0.19	3.06±0.11	3.28±0.12
1.0	6.08±0.15	7.07±0.18	2.64±0.08	3.06±0.11
2.0	5.19±0.18	6.69±0.16	2.12±0.07	2.80±0.09
5.0	4.41±0.16	6.11±0.15	1.73±0.04	2.47±0.08
10.0	3.88±0.12	5.79±0.13	1.23±0.03	2.30±0.06
15.0	3.57±0.11	5.63±0.16	1.04±0.06	2.23±0.04
20.0	3.38±0.10	5.58±0.14	0.82±0.02	2.18±0.05

[CTAB] = 1.0×10^{-2} mol dm^{-3}

[NaLS] = 1.0×10^{-2} mol dm^{-3}

Table. 4.13

Values of rate parameters used to simulate k_ψ-[surfactant] profile and binding constant for the alkaline hydrolytic reaction of isoproturon in NaLS and CTAB micelles.

Reaction conditions:

[Isoproturon] = 5.0×10^{-5} mol dm^{-3}

[NaOH] = 0.1 mol dm^{-3}

Temperature = 70°C

Parameters and Constants	Values	
	in NaLS	in CTAB
K_s (mol^{-1} dm^3)	10.21	240.00
k_m (mol^{-1} dm^3 s^{-1})	-	$1.43 \pm 0.26 \times 10^{-4}$
β	-	0.80
K_{OH^-/Br^-}	-	6.00
cmc (mol dm^{-3})	8.32×10^{-3}	8.04×10^{-4}

Table. 4.14

Values of rate parameters used to simulate k_ψ- [surfactant] profile and binding constant for the alkaline hydrolytic reaction of fenuron in NaLS and CTAB micelles.

Reaction conditions:

[Fenuron] = 5.0×10^{-5} mol dm^{-3}

[NaOH] = 0.1 mol dm^{-3}

Temperature = 80°C

Parameters and Constants	Values	
	in NaLS	in CTAB
K_s (mol^{-1} dm^3)	18.00	220.00
k_m (mol^{-1} dm^3 s^{-1})	-	$1.52 \pm 0.24 \times 10^{-4}$
β	-	0.80
$K_{OH^-/Br}$	-	6.00
cmc (mol dm^{-3})	8.61×10^{-3}	8.26×10^{-4}

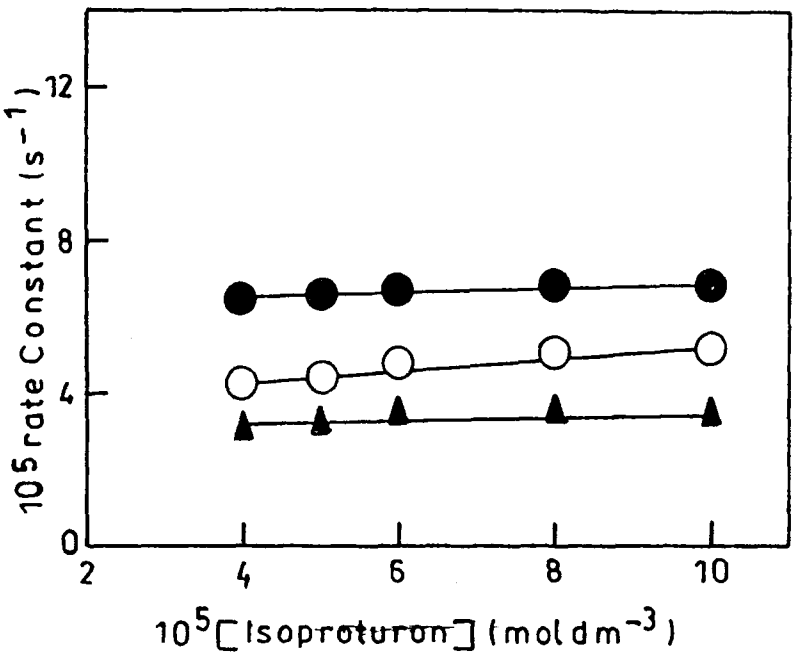


Figure 4.1 Effect of variation of [Isoproturon] on the values of rate constant in (o) aqueous, (•) CTAB and (▲) NaLS media.

Reaction Conditions: [NaOH] = 0.1 mol dm^{-3}; [CTAB] =2.0 × 10^{-2} mol dm^{-3} and [NaLS] =2.0×10^{-2} mol dm^{-3} at 70°C.

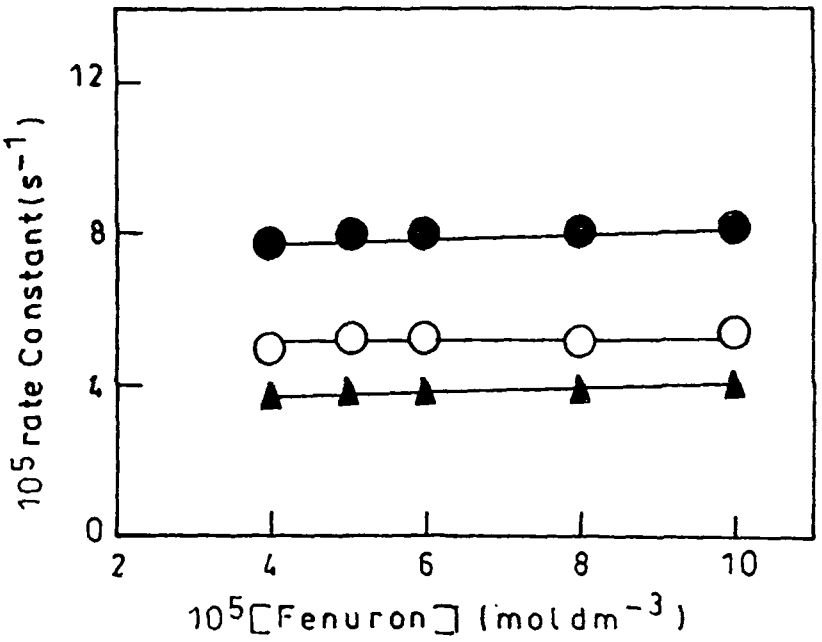


Figure 4.2 Effect of variation of [Fenuron] on the values of rate constant in (o) aqueous, (•) CTAB and (▲) NaLS media.

Reaction Conditions: [NaOH] = 0.1 mol dm^{-3}; [CTAB] =1.0 × 10^{-2} mol dm^{-3} and [NaLS] =1.0×10^{-2} mol dm^{-3} at 80°C.

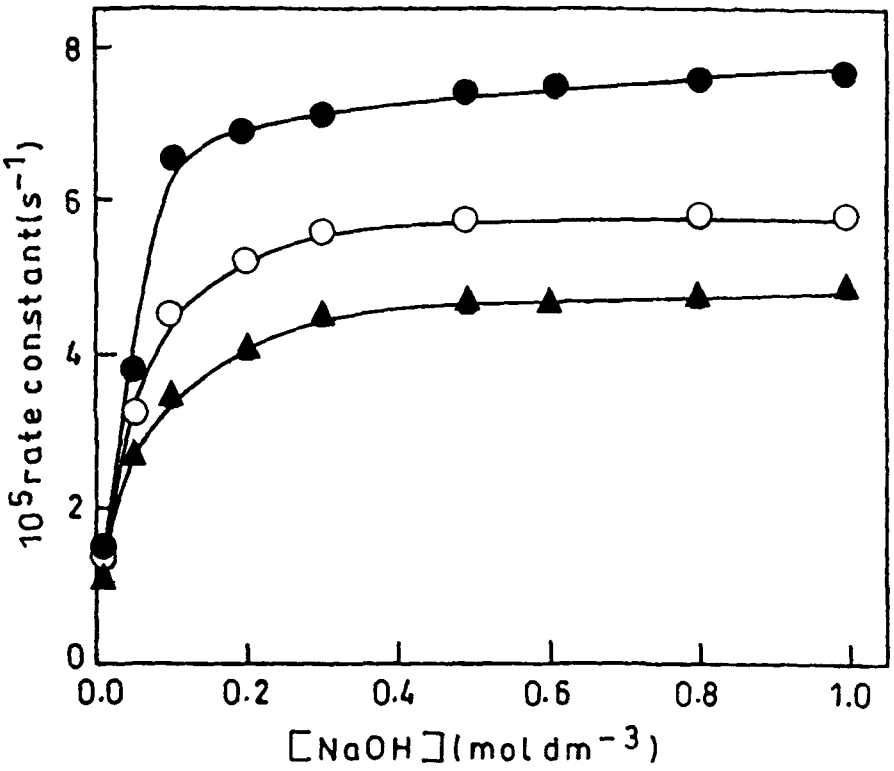


Figure 4.3 Effect of variation of [NaOH] on the values of rate constant in (o) aqueous, (•) CTAB and (▲) NaLS media.

Reaction Conditions: [Isoproturon] = 5.0×10^{-5} mol dm^{-3}; [CTAB] =2.0×10^{-2} mol dm^{-3} and [NaLS] =2.0×10^{-2} mol dm^{-3} at 70°C.

Fig

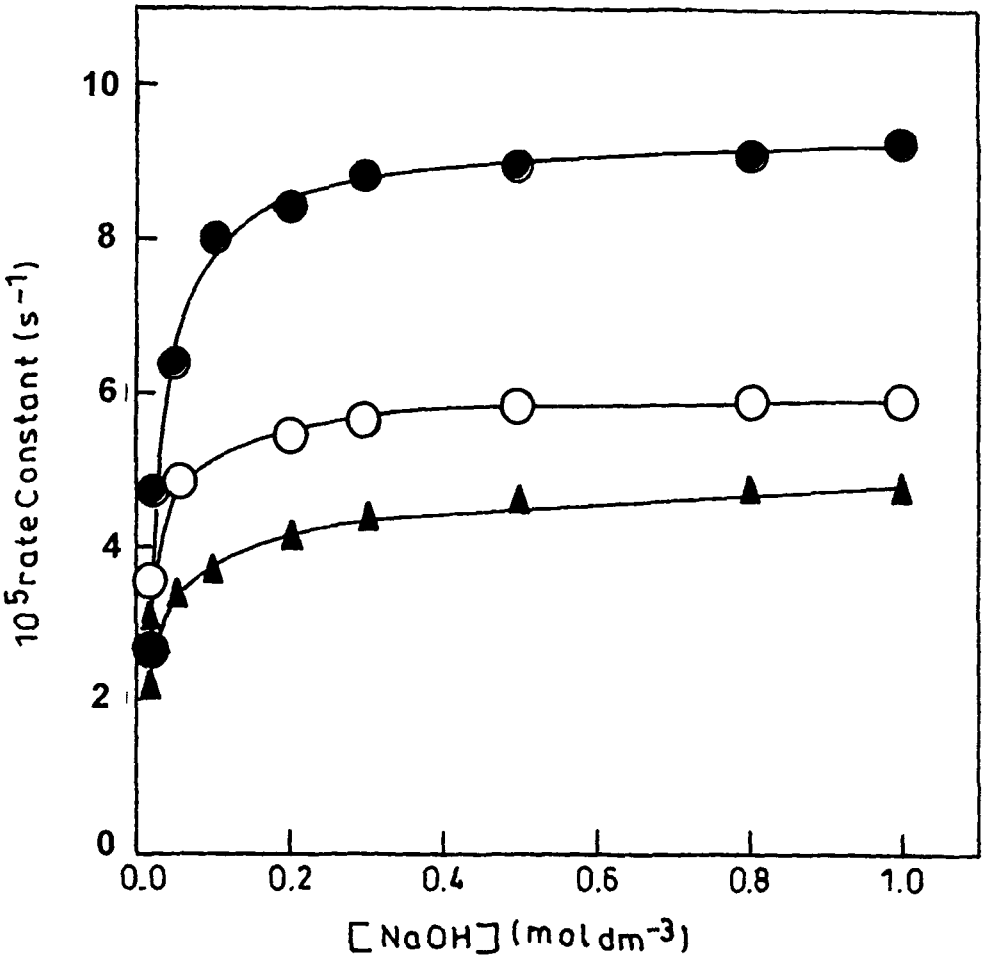


Figure 4.4 Effect of variation of [NaOH] on the values of rate constant in (o) aqueous, (•) CTAB and (▲) NaLS media.

Reaction Conditions: [Fenuron] = 5.0×10^{-5} mol dm^{-3}; [CTAB] =1.0×10^{-2} mol dm^{-3} and [NaLS] =1.0×10^{-2} mol dm^{-3} at 80°C.

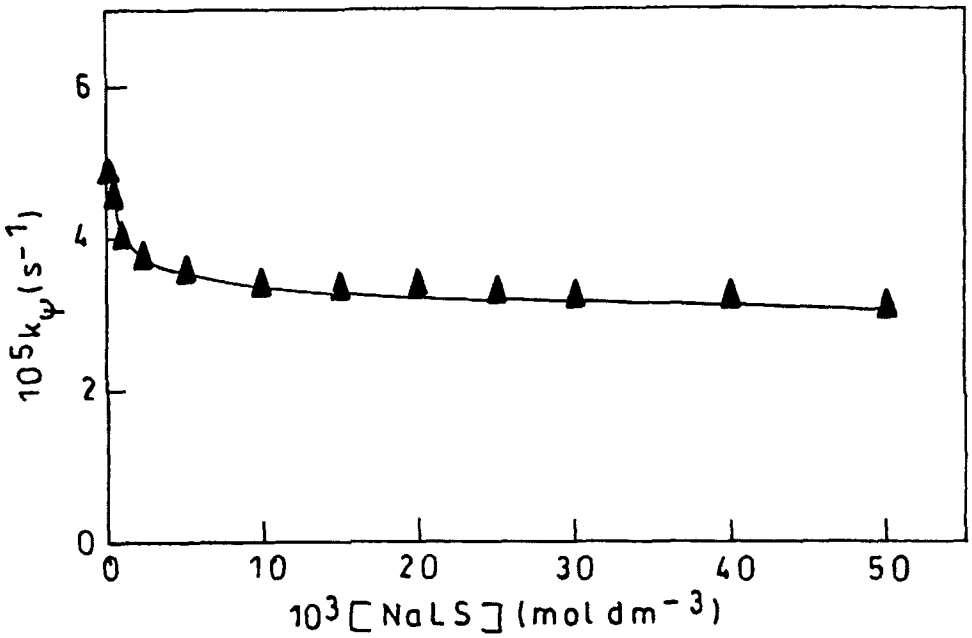


Figure 4.5 Effect of variation of [NaLS] on the values of rate constant (k_ψ).

Reaction Conditions: [Isoproturon] = 5.0×10^{-5} mol dm^{-3} and [NaOH] = 0.1 mol dm^{-3} at 70°C.

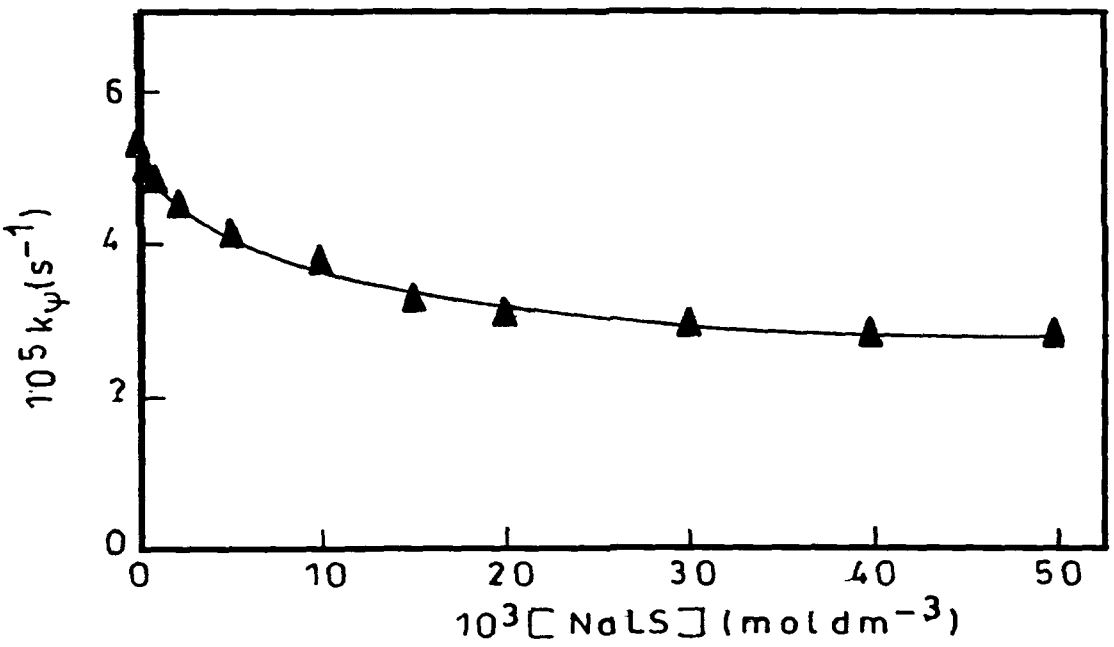


Figure 4.6 Effect of variation of [NaLS] on the values of rate constant (k_ψ).

Reaction Conditions: [Fenuron] = 5.0×10^{-5} mol dm^{-3} and [NaOH] =0.1 mol dm^{-3} at 80°C.

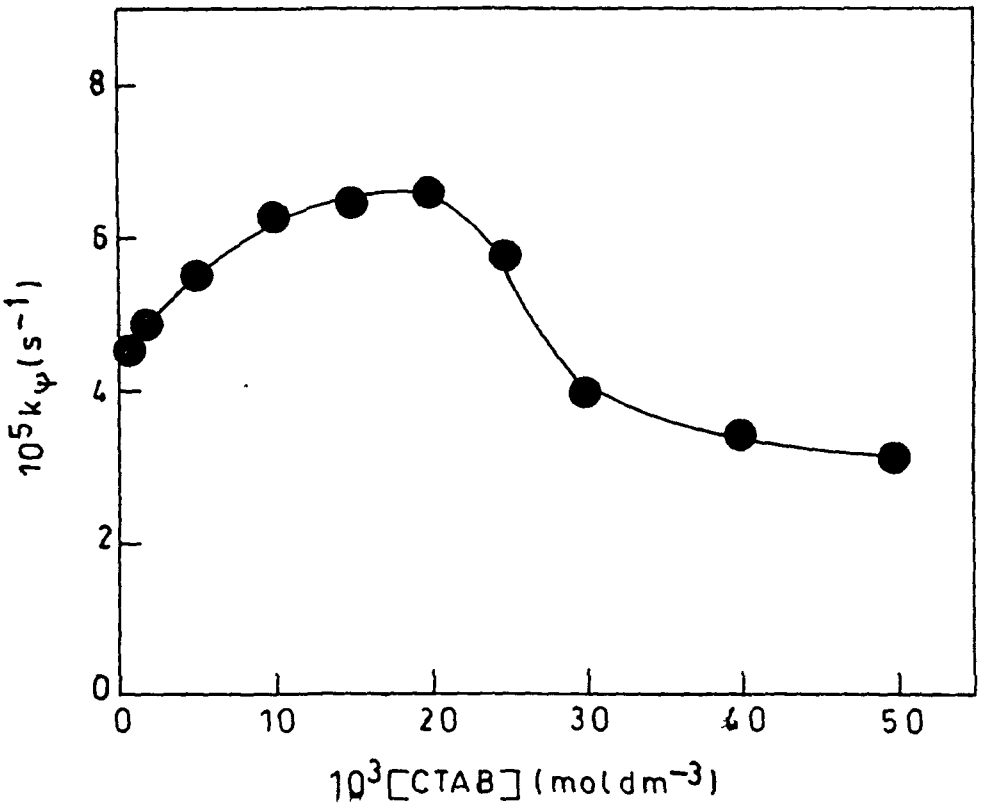


Figure 4.7 Effect of variation of [CTAB] on the values of rate constant (k_ψ).

Reaction Conditions: [Isoproturon] = 5.0×10^{-5} mol dm^{-3} and [NaOH] =0.1 mol dm^{-3} at 70°C.

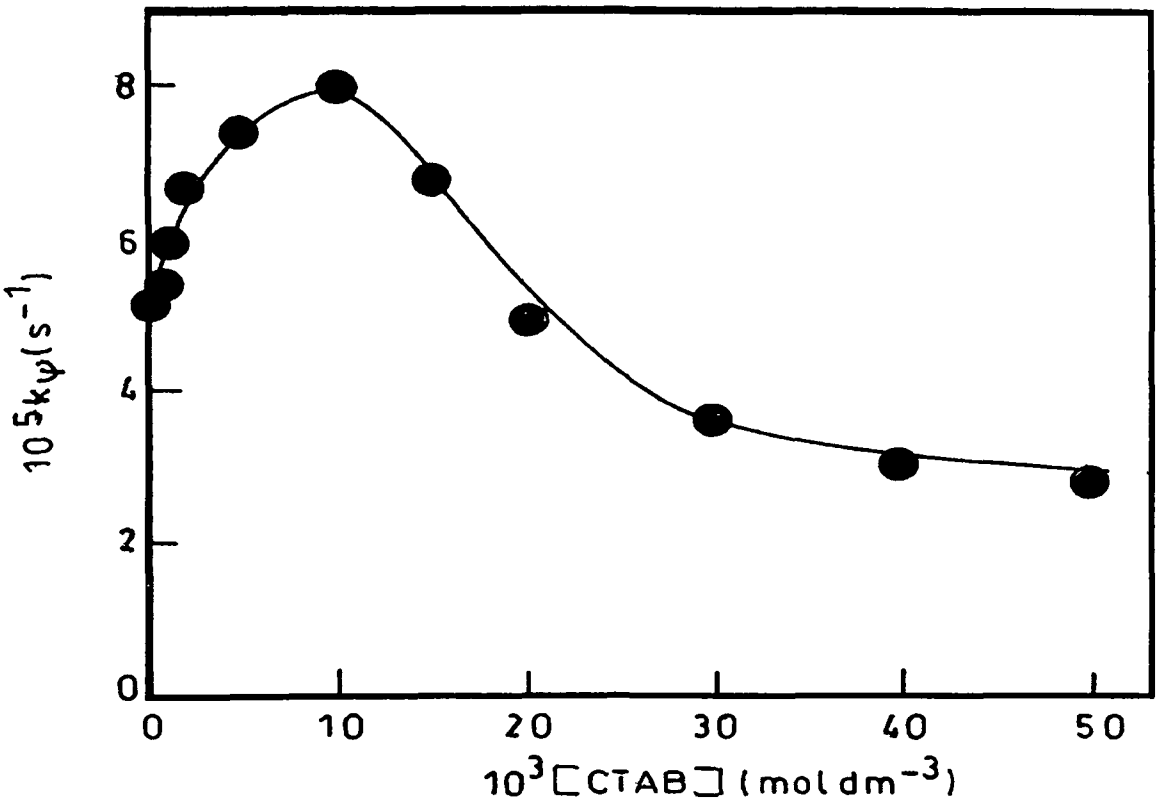


Figure 4.8 Effect of variation of [CTAB] on the values of rate constant (k_ψ).

Reaction Conditions: [Fenuron] = 5.0×10^{-5} mol dm^{-3} and [NaOH] =0.1 mol dm^{-3} at 80°C.

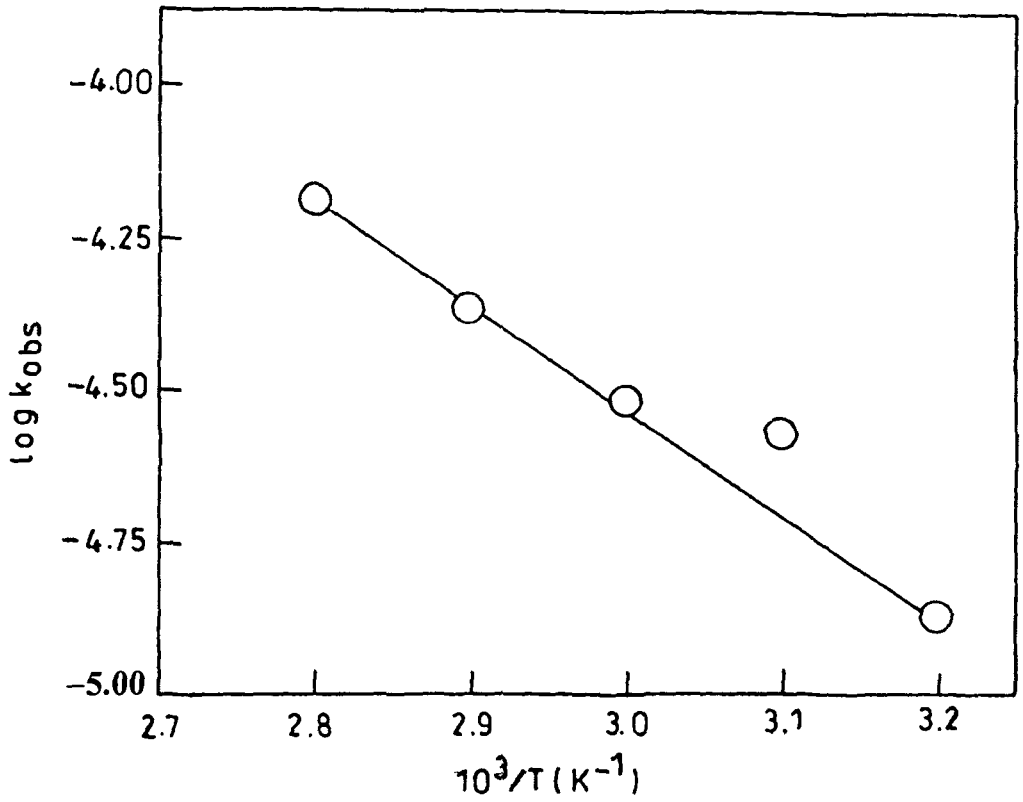


Figure 4.9 Arrhenius plot for alkaline hydrolysis of isoproturon in aqueous medium.

Reaction Conditions: [Isoproturon] = 5.0×10^{-5} mol dm^{-3} and [NaOH] =0.1 mol dm^{-3}.

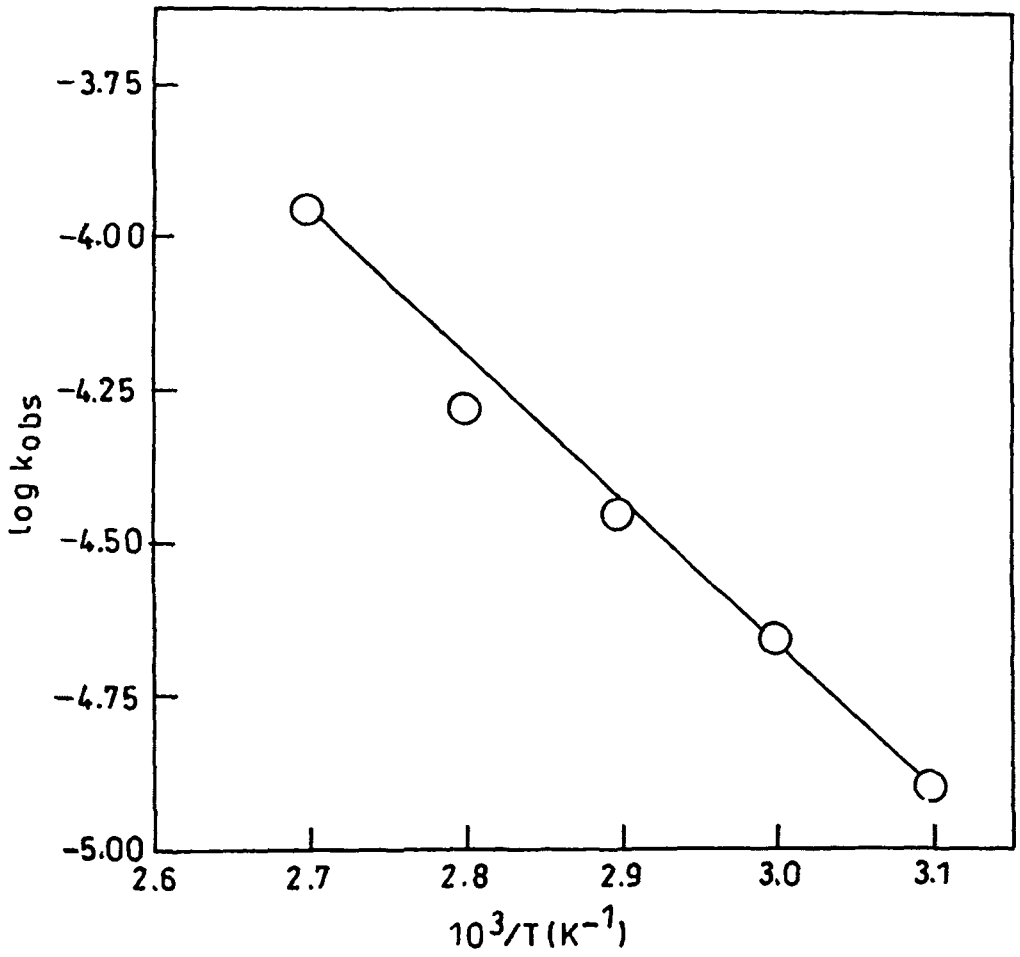


Figure 4.10 Arrhenius plot for alkaline hydrolysis of fenuron in aqueous medium.

Reaction Conditions: [Fenuron] = 5.0×10^{-5} mol dm^{-3} and [NaOH] =0.1 mol dm^{-3}.

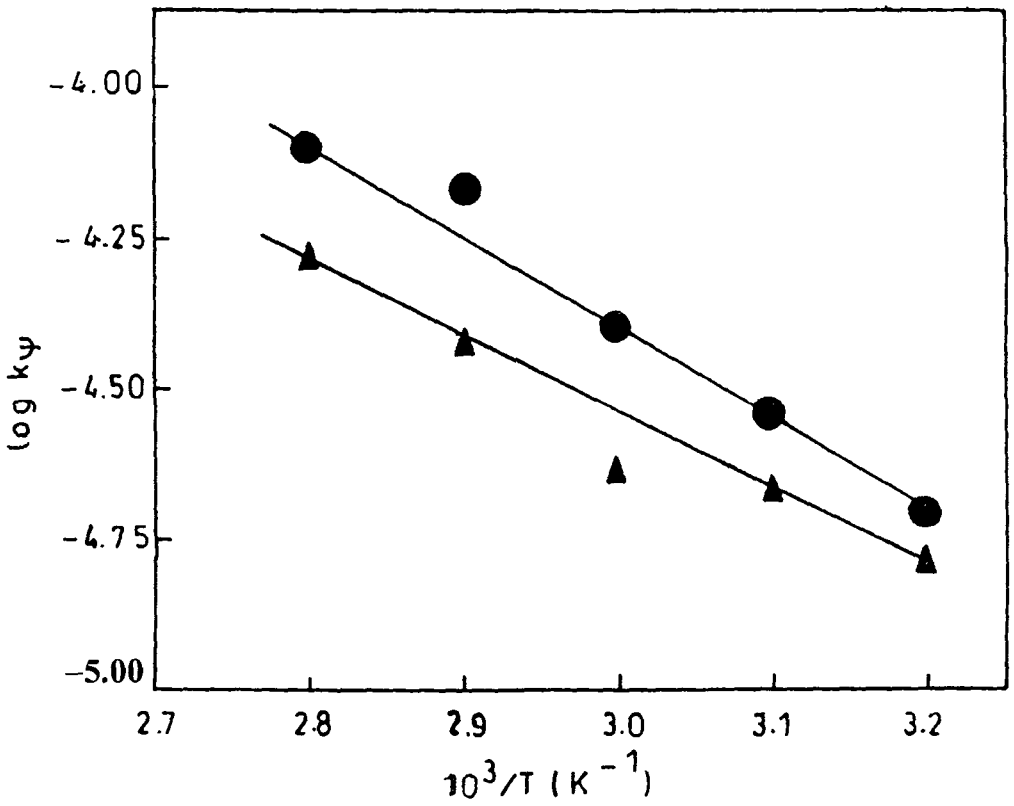


Figure 4.11 Arrhenius plot for alkaline hydrolysis of isoproturon in (•) CTAB and (▲) NaLS micelles.

Reaction Conditions: [Isoproturon] = 5.0×10^{-5} mol dm^{-3}; [NaOH] =0.1 mol dm^{-3} ;[CTAB] = 2.0×10^{-2} mol dm^{-3} and [NaLS] = 2.0×10^{-2} mol dm^{-3}.

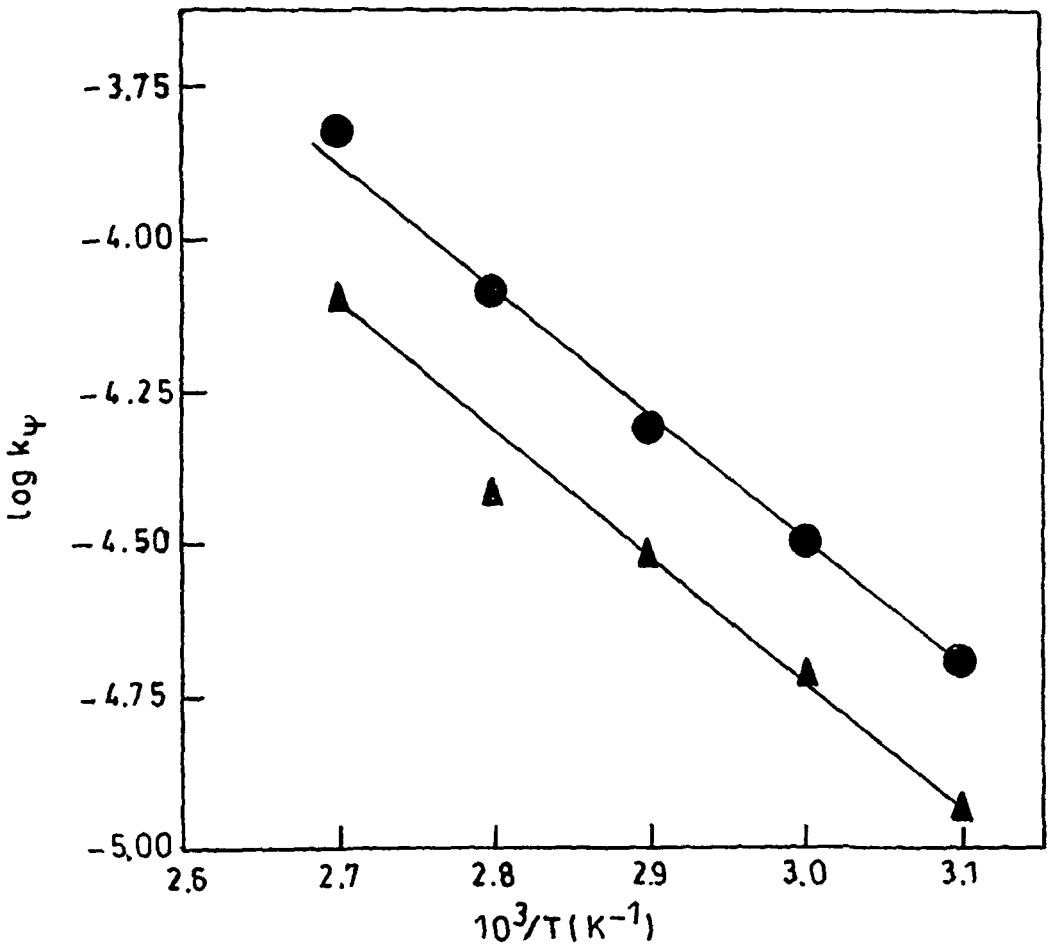


Figure 4.12 Arrhenius plot for alkaline hydrolysis of fenuron in (•) CTAB and (▲) NaLS micelles.

Reaction Conditions: [Fenuron] = 5.0×10^{-5} mol dm^{-3}; [NaOH] =0.1 mol dm^{-3}; [CTAB] =1.0×10^{-2} mol dm^{-3} and [NaLS] =1.0×10^{-2} mol dm^{-3}.

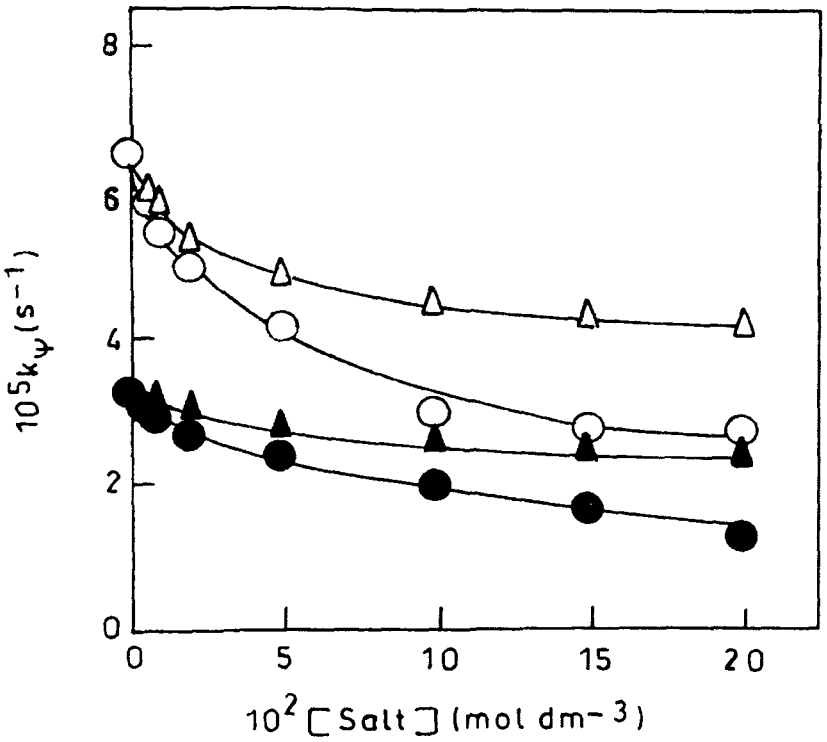


Figure 4.13 Effect of variation of [NaCl] and [KNO_3] on the values of rate constant, k_ψ (Δ, o) for KNO_3 and NaCl respectively for [CTAB] and (▲, ●) for KNO_3 and NaCl respectively for [NaLS].

Reaction Conditions: [Isoproturon] = 5.0×10^{-5} mol dm^{-3}; [NaOH] = 0.1 mol dm^{-3}; [CTAB] = 2.0×10^{-2} mol dm^{-3} and [NaLS] = 2.0×10^{-2} mol dm^{-3} at 70°C.

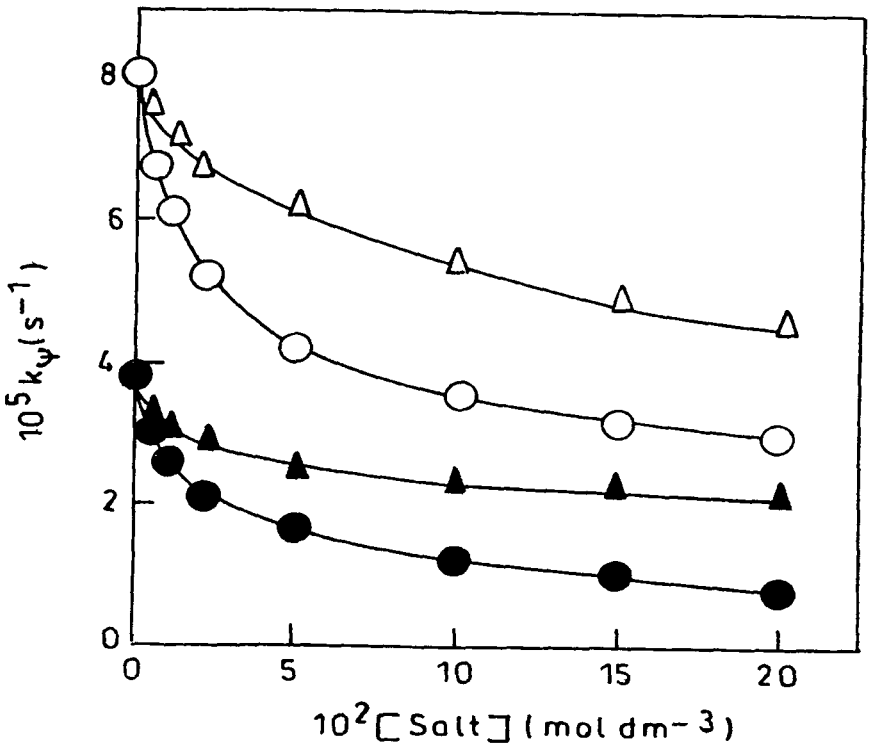


Figure 4.14 Effect of variation of [NaCl] and [KNO_3] on the values of rate constant, k_ψ (Δ, o) for KNO_3 and NaCl respectively for [CTAB] and (▲, •) for KNO_3 and NaCl respectively for [NaLS].

Reaction Conditions: [Fenuron] = 5.0×10^{-5} mol dm^{-3}; [NaOH] =0.1 mol dm^{-3}; [CTAB] =1.0×10^{-2} mol dm^{-3} and [NaLS] =1.0×10^{-2} mol dm^{-3} at 80°C.

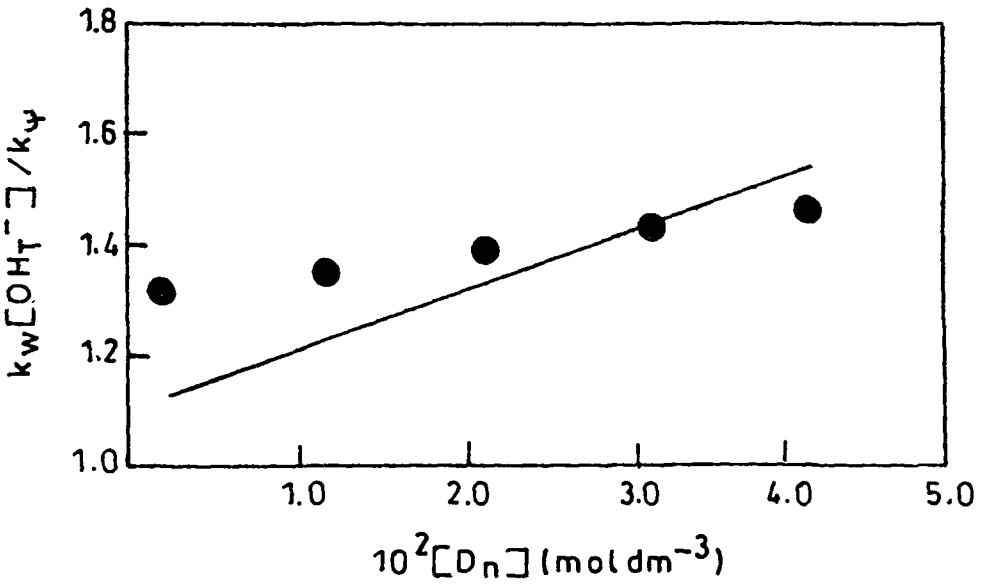


Figure 4.15 Plot of $\frac{k_w[OH_T^-]}{k_\psi}$ versus $[D_n]$

Reaction Conditions: [Isoproturon] = 5.0×10^{-5} mol dm^{-3} and [NaOH] = 0.1 mol dm^{-3} at 70°C

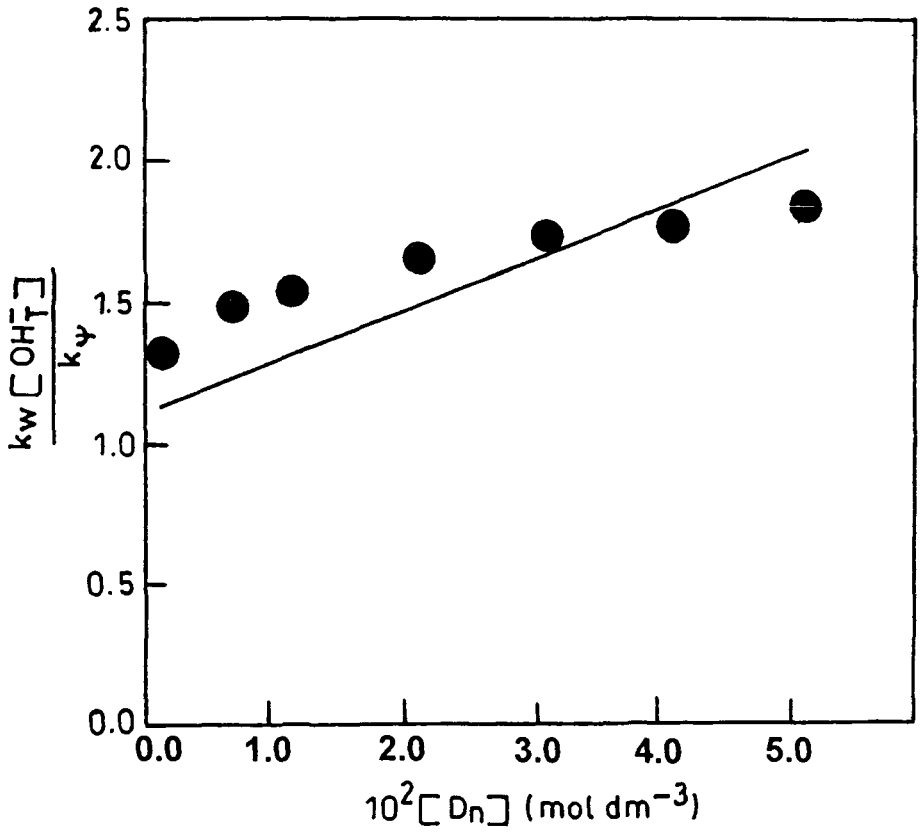


Figure 4.16 Plot of $\frac{k_w[OH_T^-]}{k_\psi}$ versus $[D_n]$

Reaction Conditions: [Fenuron] = 5.0×10^{-5} mol dm^{-3} and [NaOH] = 0.1 mol dm^{-3} at 80°C.

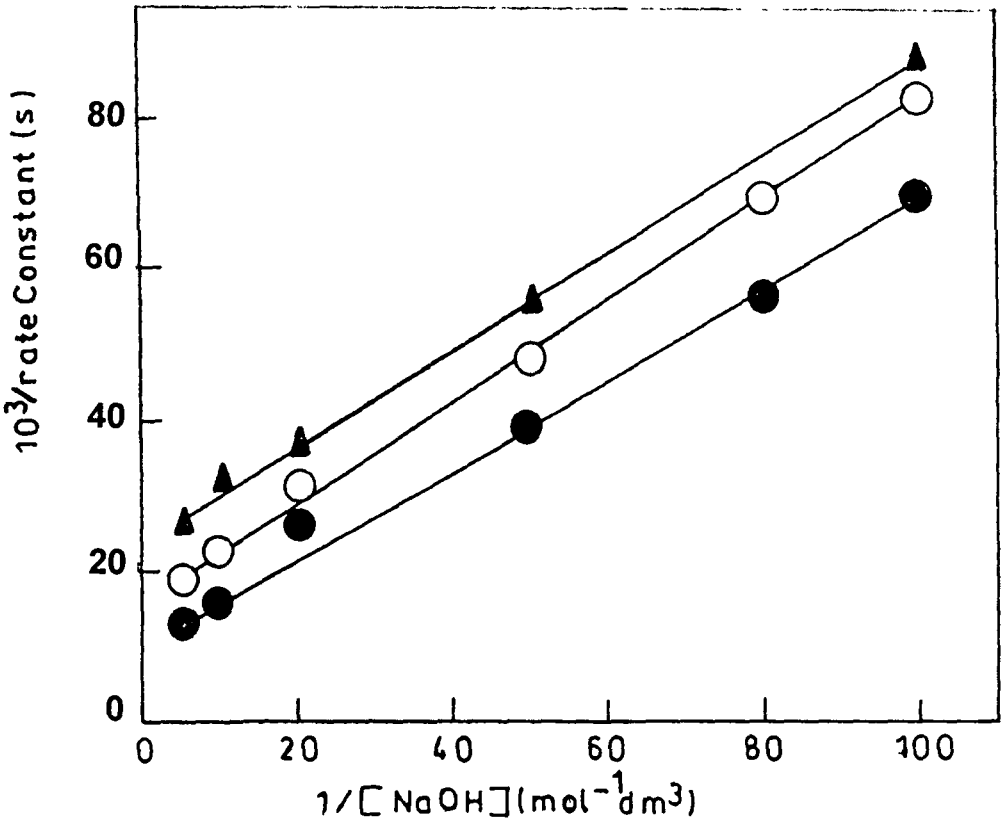


Figure 4.17 Plot of $\frac{1}{[NaOH]}$ versus $\frac{1}{\text{rate constant}}$ for (o) aqueous, (•) CTAB and (▲) NaLS.

Reaction Conditions: [Isoproturon] = 5.0×10^{-5} mol dm^{-3}; [CTAB] = 2.0×10^{-2} mol dm^{-3} and [NaLS] =2.0×10^{-2} mol dm^{-3} at 70°C.

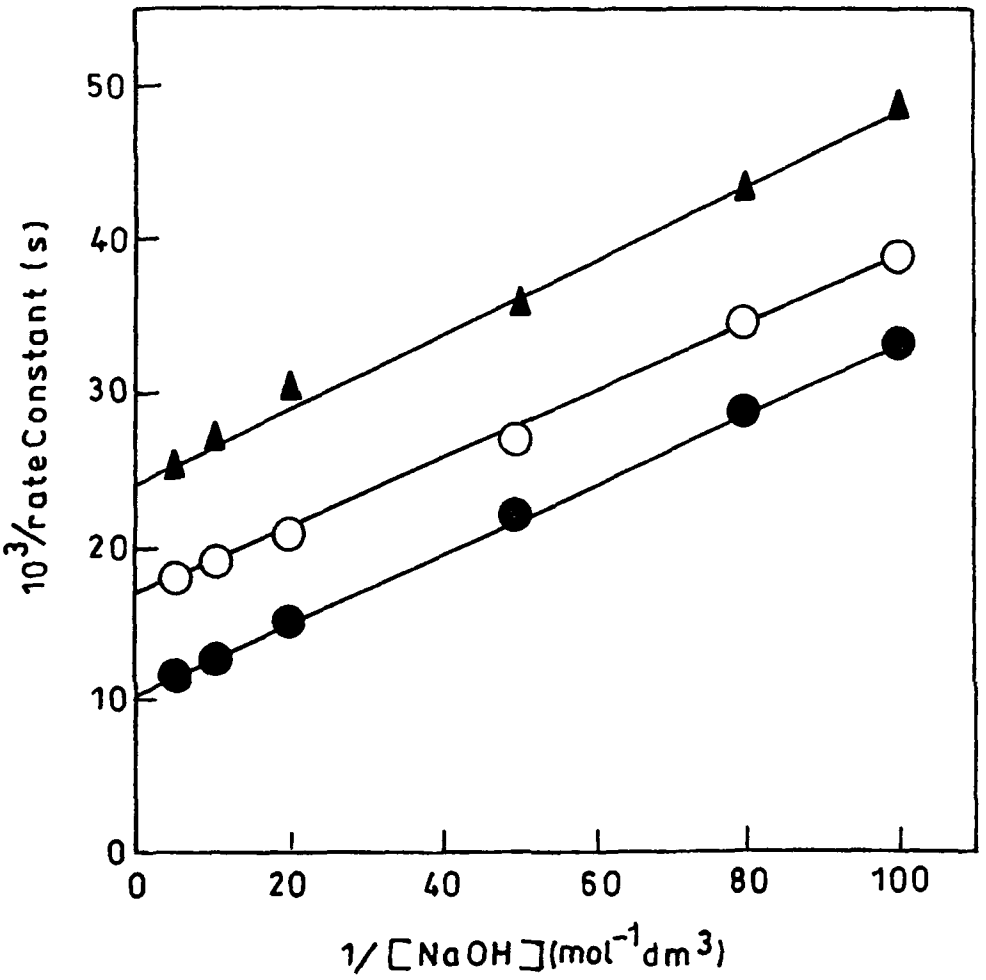


Figure 4.18 Plot of $\frac{1}{[NaOH]}$ versus $\frac{1}{\text{rate constant}}$ for (o) aqueous, (•) CTAB and (▲) NaLS.

Reaction Conditions: [Fenuron] = 5.0×10^{-5} mol dm^{-3}; [CTAB] = 1.0×10^{-2} mol dm^{-3} and [NaLS] = 1.0×10^{-2} mol dm^{-3} at 80°C.

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Polarographic study on parathion in micellar media

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Direct current polarographic study of parathion shows two reduction waves at pH 3.0–10.0. The second wave does not appear in highly alkaline medium due to the stable nature of hydroxylamine. Two waves also appear at pH 3.0–10.0 in presence of anionic surfactant, sodium dodecyl sulphate (SDS) as well as nonionic surfactant, Triton X-100. Half wave potential increases with increasing concentration of SDS while it decreases with increasing concentration of Triton X-100. The second reduction wave does not appear even at pH 3.0–10.0 in presence in cationic surfactant, cetyltrimethylammonium bromide (CTAB). Half wave potential increases slightly with increasing concentration of CTAB.

Several chemicals[1] are being used to control pests in agriculture, public health, forestry, veterinary practices. Organophosphates are widely used as broad spectrum insecticides, acricides, fumigants and nematicides. Organophosphates are non-systemic pesticides which contact stomach and respiratory action (cholinesterase inhibitor). Thus chemical crop protection is a profit induced poisoning process which affects our lives and economy. The migration of pesticides into various compartments of environment has generated public awareness concerning their fate and toxic effects. It is known that the surfactant is one of the important additives used in pesticides formulations, in order (i) to increase the solubility of the pesticide in aqueous medium, (ii) to stabilize the pesticide by controlling evaporation or decomposition (above CMC), (iii) to enhance the effectiveness of the pesticide by providing the fine spray (lower CMC) and (iv) studies in micellar media are helpful in exploring the mode of action of pesticides (redox behaviour) in biomacromolecular ensembles, (e.g. enzymes).

Amongst analytical methods used for pesticides, polarography has been found to be more sensitive, selective and reproducible. A good polarogram is obtained for pesticides containing an oxidisable or reducible group such as nitro, halogen, carbonyl etc. Pesticides not containing such a group can usually be determined by formation of a suitable derivatives. A few recently reported papers on this subject are summarized in the following paragraphs. Therefore there is a genuine interest in electrochemical studies of pesticide in micellar media.

Garcia *et al.*[2] have reported a polarographic study of the organochlorine pesticides, dieldrin, endosulfan and endosulfan sulphate in micellar solution. The best analytical signal to noise ratio was found in a mixture of Hyamine 2389 and Triton X-405 at pH 6. The pesticides can be determined in micellar solution by differential pulse polarography (DPP) using pulse amplitude, ΔE of –50 mV, over the range 1.0×10^{-6} mol L^{-1} simultaneous analysis was based on hydrolysis of endosulfan and endosulfan sulphate in basic medium. Galvez *et al.*[3] have reported a polarographic study of the reduction of herbicide, simazine, in solution of an anionic surfactants, sodium pentane sulphonate. In this case two reduction peaks were observed in differential pulse polarography (DPP) below pH 2.0. Whereas only one peak was obtained above pH 2.0. DP polarogram of simazine in oil water emulsion showed only one peak even at pH less than 2.0, suggesting that the pesticide hydrolysis was hindered in the emulsified medium. The limiting current in diffusion controlled and the electrode process was irreversible. The diffusion coefficient of simazine in emulsified medium is 8.85×10^{-6} cm^2 s^{-1} and αn_a and K_f^0 (defined later) are 0.82 and 8.03×10^{-14} cm s^{-1} respectively. Simazine was determined in a spiked irrigation water over the concentration range 8.0×10^{-7}–4.0×10^{-5}. The limit of detection was 2.2×10^{-7} mol L^{-1}. Tandon *et al.*[4] have reported two well defined diffusion controlled waves of dichloro diphenyl dichloroethane (DDD) and benzene hexa chloride (BHC) at pH 7 in micellar medium. However polarographic studies have not been reported on parathion in micellar media.

Therefore, it was thought to be worth while to make po-

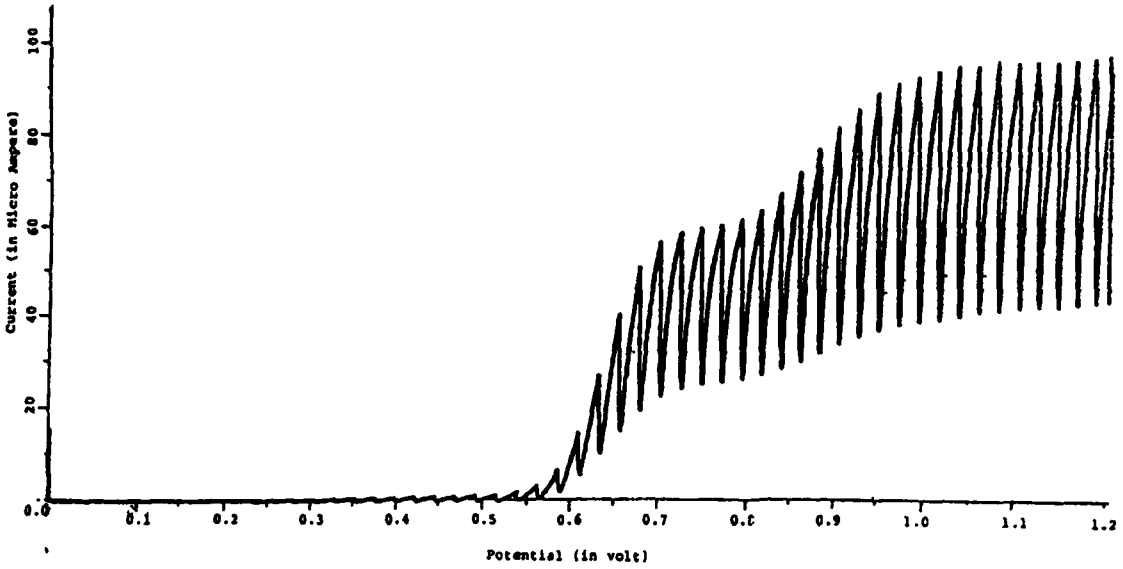


Fig. 1 Typical polarogram of parathion (1×10^{-4} mol dm^{-3}) in acetate buffer at 25°C

larographic study of parathion in micellar medium. The results obtained are described in this paper.

Results and discussion

A typical polarogram (Fig. 1) of using acetate buffer (pH 4.8) gives two reduction waves with $E_{1/2}$ value at –0.657 V and –0.94 V. The reduction was of diffusion controlled in nature. It was confirmed by studying the height of reduction wave at varying height of mercury column (h) over the orifice of capillary. For the logarithmic analysis of the wave, the following equation was used and E_{de} was plotted against log $[i/(i_d - i)]$

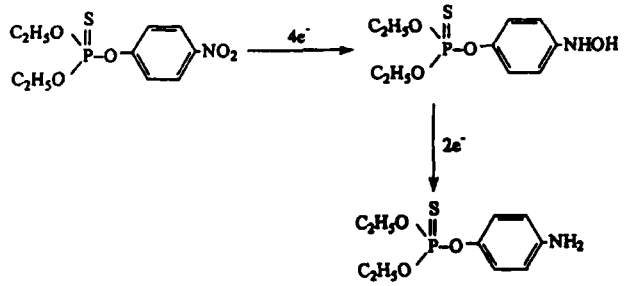
$$E_{de} = \frac{0.0591}{\alpha n_a} \log \left(\frac{1.349 k_{f,h} t^{1/2}}{D_0^{1/2}} \right) - \frac{0.0542}{\alpha n_a} \log \frac{i}{i_d - i}$$

where, α = transfer coefficient, n_a = number of electron involved in reduction process, $k^0_{f,h}$ = potential dependent heterogeneous rate constant, t = drop time, D_0 = diffusion coefficient of electroactive substance, i = current and i_d = diffusion current.

The first term on the right hand side of this equation is equal to $E_{1/2}$ and the above equation can be written as

$$E_{de} = E_{1/2} - \frac{0.0542}{\alpha n_a} \log \frac{i}{i_d - i}$$

The plot of E_{de} vs log $[i/(i_d - i)]$ gave straight lines (Fig. 2) with slope 0.015 and 0.014 and intercepts at –0.657 V and –0.964 V. The first wave appears due to 4-electron reduction of nitrogroup of parathion into hydroxylamine and the second wave appear due to 2-electron reduction of hydroxylamine to amine. The following is the mechanism of successive reduction at dme (Scheme 1).



Scheme 1

The difference in the value of $E_{3/4}$ and $E_{1/4}$ attributes to the irreversibility of the reduction of parathion in buffer and micellar media. The difference in $E_{3/4}$ and $E_{1/4}$ is larger than the theoretical value expected for 4-electron and 2-electron reversible reduction. The irreversibility was also confirmed by studying the dependence of current on h_{corr} at different state of the wave. The current was independent of h_{corr} at the foot of the wave, whereas it was proportional to $h^{1/2}_{corr}$ at the plateaue of the wave.

Effect of surfactants :

Fig. 3 shows the effect of varying concentration of Triton X-100 (1×10^{-2}–5×10^{-2} mol dm^{-3}) at constant concentration of parathion (1×10^{-4} mol dm^{-3}) and pH 4.8. It shows that the value of half-wave potential ($E_{1/2}$) for both waves decreases with increasing concentration of Triton X-100. Fig. 3 shows the effect of varying concentration of SDS (1×10^{-2}–5×10^{-2} mol dm^{-3}) at constant concentration of parathion (1×10^{-4} mol dm^{-3}) and pH 4.8. In this case $E_{1/2}$ increases sharply with increasing concentration of SDS. Fig. 3 shows the effect of varying concentration of CTAB (1×10^{-2}–5×10^{-2} mol dm^{-3}) at constant concentra-

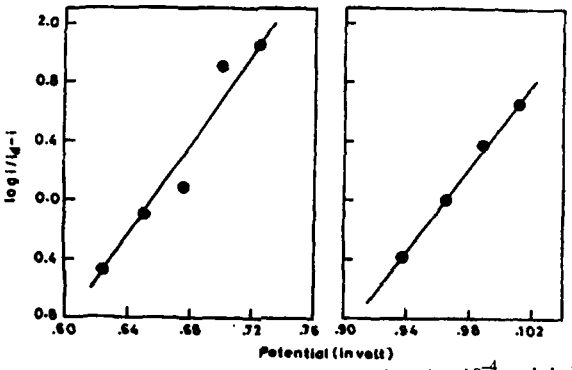


Fig. 2. Plot of E_{de} vs log $[i/(i_d - i)]$ for parathion (1×10^{-4} mol dm^{-3}) in acetate buffer (pH 4.8) at 25°C.

tion of parathion (1×10^{-4} mol dm^{-3}) and pH 4.8. In this case only one wave i.e. the first wave was obtained while the second wave disappeared completely. The $E_{1/2}$ of the first wave increases slightly with increasing concentration of CTAB.

The plot of E_{de} vs log $[i/(i_d - i)]$ was used to calculate the kinetic parameter αn_a and $k_{f,h}$ for each concentration of surfactants. A decreases in αn (3.7–3.3) was observed with the increase in concentration of ionic surfactants (SDS and CTAB). However, reversal was observed in case of non-ionic surfactants (TX-100). The decreases in α-value suggests that the irrever sible reduction of parathion at dme becomes more difficult with increasing concentration of ionic surfactants while in the presence of TX-100 reduction of parathion is less difficult. The variation in the value of $k_{f,h}$ exhibits irreversible reduction of parathion in presence of TX-100 and difficult in ionic surfactants.

The above mentioned effect of the surfactant on the electrochemical nature of parathion is either due to the adsorption of the molecule at the electrode surface prior to reduction or due to decrease in the rate of electron transfer causes by the adsorption of the surfactant.

Effect of pH :

The reduction behaviour of parathion was studied at pH 3.0–12.0. The concentrations of parathion (1×10^{-4} mol dm^{-3}), surfactants (1×10^{-4} mol dm^{-3}) and potassium nitrate (1×10^{-2} mol dm^{-3}) were kept constant, pH was adjusted by adding NaOH and HCl solutions. Two waves were found in the presence of Triton X-100 at pH range 3.0–10.0 while only first wave was found at pH 10.40–12.00. The half wave potential of the first wave increases with increasing pH 3.0–10.0 and then it remains constant in the pH range 10.40–12.00. Similar behaviour was also observed on adding SDS. In presence of CTAB, only the first wave was obtained at pH 3.0–12.0 and its $E_{1/2}$ increases sharply with increasing pH.

The aforesaid results show that in acidic or mild basic medium (pH 3.0–10.0) parathion reduces to hydroxylamine and then to amine so two waves appear and in basic medium (pH 10.40–12.00) hydroxylamine is quite stable or does not reduce to amine so only the first wave appears. These findings are in line with the following results reported in the literature.

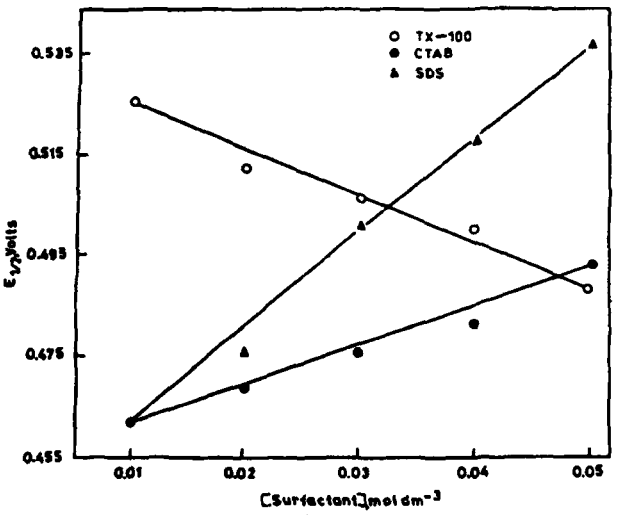


Fig. 3. Plot of [surfactant] vs $E_{1/2}$ for parathion (1×10^{-4} mol dm^{-3}) and at pH 4.8.

DP polarographic studies[3] on simazine show that the high concentration (>0.01%) of cationic and non-ionic surfactants suppressed the peak in the entire pH range. While the anionic surfactants exhibited different behaviour. DC plarography of pesticides[6] containing azomethine showed that non-ionic surfactants suppressed the main wave. A mixture of Hyamine 2389 and Triton X-405 gave the best analytical signal-to-noise ratio for dieldrin, endosulfan and endosulfan sulphate by DP polarography[2]. The increasing concentration of surfactants increased the irreversible electrode reactions of DDD and BHC[4]. DC polarography[7] of pyrazoline-5-ones has shown that i_d of the second wave increased and i_d of the first wave gradually decreased with increasing concentration of surfactants.

Conclusion : The above results show that the polarography can be used successfully for routine analysis and identification of parathion in micellar media.

Experimental

Apparatus : Polarograph (264A) and omnigraphic X-Y recorder (RE 0089), dropping mercury electrode, platinum electrode and calomel electrode (KCl saturated) from Princeton USA, and Elico pH meter (LI-120, Hyderabad, India), were used.

Chemicals : Ethyl parathion (50%) (Bayer, India Ltd.),

acetic acid and sodium hydroxide (E. Merck, India), Triton X-100 and sodium dodecyl sulphate (Fluka, India). All other chemicals used were of analytical grade.

Preparation of solutions : Solution of ethyl parathion (0.01 *M*) was prepared in 50% aqueous methanol. Acetate buffer was prepared as usual[5]. Solution of potassium nitrate (0.1 *M*), hydrochloric acid and sodium hydroxide (0.01 *M*), cetyltrimethylammonium bromide, Triton X-100 and sodium dodecyl sulphate (0.1 *M*) were prepared in doubly distilled water (DW)

Procedure : Acetate buffer or sodium hydroxide solution or diluted hydrochloric acid, ethyl parathion solution and surfactant were placed in a cell, which was thermostated at 25°C. The total volume of the solution was made up to 10 ml. The inert atmosphere was ensured by passing nitrogen gas (purified after bubbling through alkaline pyrogallol solution) through the solution for about 10 min, and then the corresponding polarograms were recorded between 0.0 to −1.5 V with a pulse amplitude of 50 mV and a scan rate of 10 mV s^{-1}.

Acknowledgement

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SHORT COMMUNICATION

Kinetics of the acid hydrolysis of isoproturon in the absence and presence of sodium lauryl sulfate micelles

S. K. Gangwar · M. Z. A. Rafiquee

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Abstract Kinetics of the hydrolysis of isoproturon by hydrochloric acid has been studied spectrophotometrically in the absence and the presence of anionic sodium lauryl sulfate (NaLS) micelles The anionic micelle was found to increase the rate of reaction The reaction followed first-order kinetics with respect to isoproturon and was linearly dependent upon [HCl] In both aqueous and micellar pseudophases the reaction was started with the protonation of the amino group of isoproturon followed by attack of water to yield phenylcarbamic acid and the corresponding amine, thus obeying the addition–elimination mechanism The surfactant decreased the activation entropy The binding constant in consistence with the rate constants was evaluated on the basis of pseudophase ion-exchange model The added salts (NaCl and KCl) decreased the rate of reaction due to the exclusion of H^+ from micellar surfaces

Keywords Surfactant Sodium lauryl sulfate Isoproturon Hydrolysis

Introduction

Micelles and other association colloids such as reverse micelles and microemulsions, are dynamic aggregates of non-ionic ionic or zwitterionic surfactants that form transparent and thermodynamically stable solutions [1, 2] These aggregates find a variety of important commercial applications like tertiary oil recovery [3], formulations in cleaning products [4], solubilization and stabilization of oils and flavours in food products [5] Association colloids are also commonly used in the formulations of pesticides and herbicides in agriculture [6] Micellar media are regarded as model systems for the compartmentalizing and organizing ability of biological membranes and the catalytic activity of enzymes [7–9] Micelles act as microreactors and influence chemical reactivity primarily by binding or excluding reactants and secondarily by changing the free energy of activation [10–12] In bimolecular reactions aggregate effects on chemical reactivity are generally interpreted by using pseudophase models, which treat micelles and water as separate reaction media The enhancement in the rate of reactions is attributed to the binding and concentrating the reactants in the very much smaller volume of micellar pseudophase, i e within the Stern layer's region Inhibition is explained on the basis of the compartmentalization of reactants

The hydrolysis of isoproturon and other phenylureas [13 15] has been a subject of increasing interest These molecules are used as efficient herbicides in agriculture and possess distinctive aspects of reaction mechanism Isoproturon is a hydrophobic substrate slightly soluble in water and has a polar reactive group It is hydrolysed in both acidic and basic media In acidic media the reaction proceeds through the protonation of isoproturon followed by rate-determining attack by water, giving a tetrahedral intermediate The intermediate then decomposes to yield amine and phenylcarbamic acid Finally phenylcarbamic acid decarboxylates under acidic condition to form the corresponding aniline (Scheme 1) The multi-step protonation and hydrolysis of isoproturon provide an interesting case to study in micellar medium

In the present work, a detailed kinetic study on the hydrolysis of isoproturon in acidic medium in the absence

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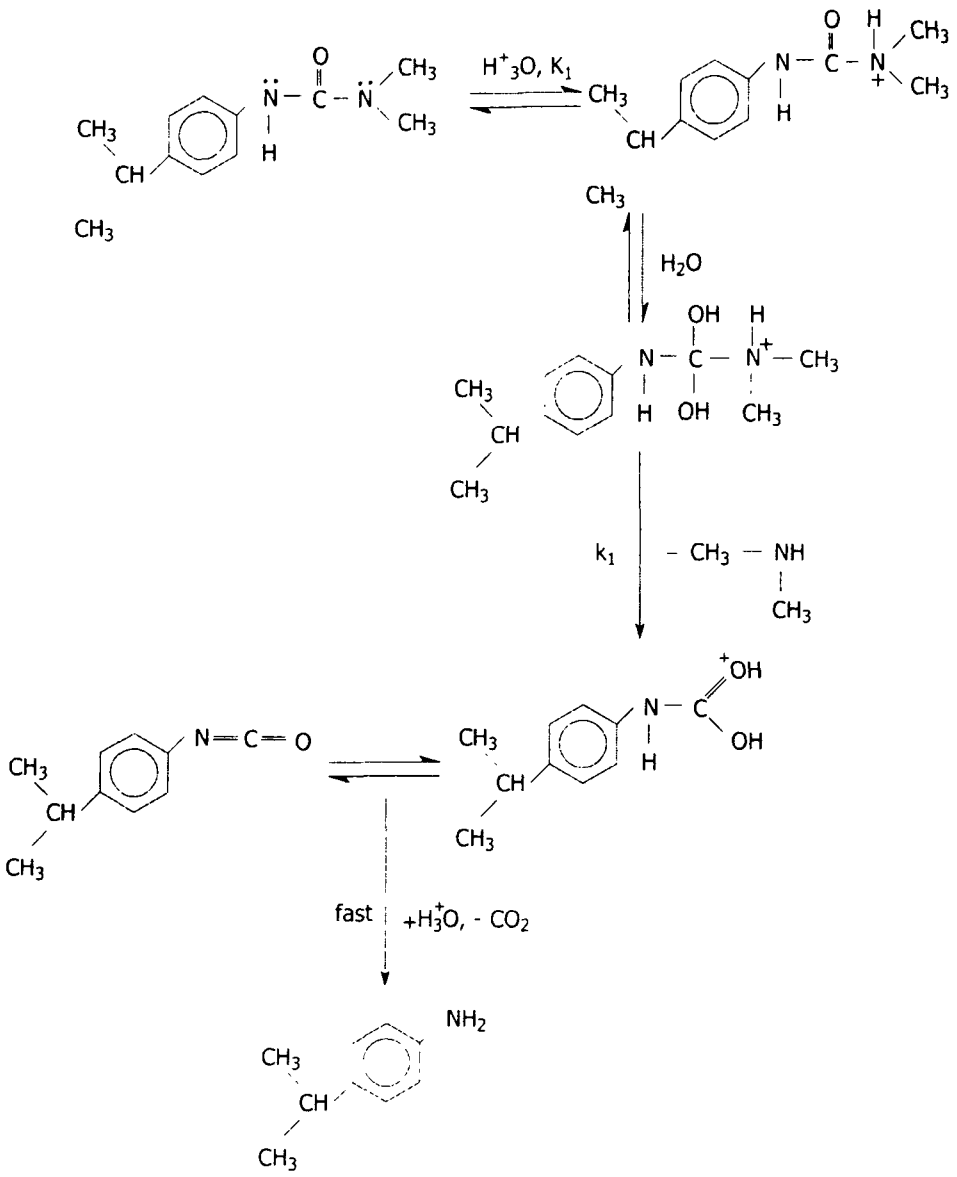
Scheme 1 Hydrolysis of isoproturon in acidic media through an addition-elimination mechanism



and presence of sodium lauryl sulfate has been carried out to study the influence of surfactant on the rate of reaction. The aim of the work also includes the understanding of the mechanism of the reaction in the presence of surfactant. The results were treated using pseudophase ion-exchange (PPIE) model [16–19], and the kinetic parameters obtained gave a good fit to the kinetic data.

Experimental

Materials

Isoproturon 3-(4-isopropyl phenyl)-1, 1-dimethyl urea (Siris Crop Sciences Limited, New Delhi, India), hydrochloric acid (E. Merck, India), methanol (Qualigens, India), sodium lauryl sulfate (CDH, India) and sodium chloride (BDH, India) were used as received. All the other salts used were of analytical reagent grade. Double-distilled and deionised water was used throughout.

Stock solutions of hydrochloric acid (1.0 mol dm^{-3}) and sodium lauryl sulfate (1.0×10^{-1} mol dm^{-3}) were prepared in distilled water and that of isoproturon (1×10^{-2} mol dm^{-3}) in methanol.

Kinetic measurements

Kinetic experiments were carried out by taking the requisite amount of isoproturon, surfactants and salts in a three-necked reaction vessel. The reaction vessel was fitted with a double-surface condenser to check any evaporation. The reaction vessel was kept in a thermostated water bath at the

desired temperature (±0.1 °C). The zero time was taken when half of the required volume of thermally equilibrated hydrochloric acid was added to the reaction vessel. Progress of the reaction was followed by measuring the absorbance at constant intervals of time on an Elico SL-164 UV-Vis Spectrophotometer using 1-cm path length quartz cuvettes. All the kinetic experiments were run under the first-order condition in which the concentrations of H^+ and surfactant were kept largely in excess over [isoproturon]. The pseudo-first-order rate constants were determined from the slope of $\ln(A-A\alpha)$ vs time, where A is the absorbance of isoproturon at λ_{max} (240 nm). The hydrolytic reaction was followed for the completion of 80% of the reaction. A non-linear least-square technique was used for the treatment of data to obtain values of the binding constant of isoproturon with sodium lauryl sulfate micelles, K_s, and second-order rate constant with sodium lauryl sulfate micelles, k_m. The best values that fit the curves were obtained from the computer program. The critical micelle concentration (CMC) of sodium lauryl sulfate containing isoproturon and hydrochloric acid were determined conductometrically at 70 °C, and its value was 8.3×10^{-3} mol dm^{-3}.

Results

Reaction in the absence of micelles

The kinetic experiments were performed at different initial concentrations of isoproturon ranging from 4.0×10^{-5} to 1.0×10^{-4} mol dm^{-3} at fixed [HCl] (1.0×10^{-1} mol dm^{-3}) at 70 °C, and the ionic strength was kept constant at 1.0 mol dm^{-3}. The values of pseudo-first-order rate constants obtained remained the same with the increase in initial concentrations of isoproturon, indicating that the order of hydrolysis is unity with respect to it. The order with respect to hydrochloric acid was deduced from the values of the rate constants obtained at several [HCl] (0.5×10^{-1} 1.5 mol dm^{-3}) at fixed ionic strength (1.0 mol dm^{-3}) and [isoproturon] (5.0×10^{-5} mol dm^{-3}). The results are given in Fig. 1. The rate of reaction was found to increase with the increase in [HCl] linearly. The rate constants were found to be independent of the ionic strength, showing that one of the reactants taking part in the hydrolysis is an uncharged molecule. The kinetic runs were also performed within the temperature range of 40–70 °C. The concentrations of HCl (1.0×10^{-1} mol dm^{-3}) and isoproturon (5.0×10^{-5} mol dm^{-3}) were kept constant, and the ionic strength was maintained at 1.0 mol dm^{-3}. The energy of activation was determined from the plot of log k_{obs} vs $1/T$. The values of other activation parameters were calculated using Arrhenius and Eyring equation and are given in Table 1.

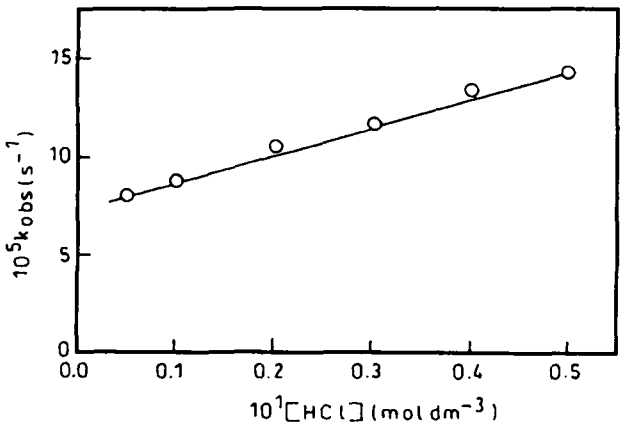


Fig. 1 Effects of [HCl] on the k_{obs}. Reaction conditions: isoproturon (5.0×10^{-5} mol dm^{-3}) at 70 °C

Reaction in the presence of sodium lauryl sulfate

It was observed that the rate of reaction was increased with the increase in [sodium lauryl sulfate, NaLS]. The effect of varying [NaLS] (1.0×10^{-3} 5.0×10^{-2} mol dm^{-3}) was studied at constant [isoproturon] (5.0×10^{-5} mol dm^{-3}) and [HCl] (1.0×10^{-1} mol dm^{-3}) at 70 °C. The values of the pseudo-first-order rate constants (k_ψ) were determined in the presence of NaLS. The plot of k_ψ vs [NaLS] is given in Fig. 2. The kinetic experiments performed in the presence of NaLS micelles show that the pseudo-first-order rate constants are independent of the initial concentrations of isoproturon. The values of rate constants increased rapidly with increase in [HCl] at lower concentrations, but it increased gradually on further increase in [HCl], as shown in Fig. 3.

Discussion

At surfactant concentrations above the CMC, k_ψ is assumed to depend upon the reactants' concentrations in each of aqueous and micellar pseudophases. The reaction occurring in each of the pseudophases is presented in Scheme 2.

Table 1 Activation parameters in absence and presence of NaLS micelles for the hydrolysis of isoproturon by hydrochloric acid

Activation parameter	In the absence of surfactant	In the presence of NaLS
E_a (kJ mol^{-1})	14.0±1.2	30.1±1.6
$\Delta H^{\neq}$ (kJ mol^{-1})	11.5±1.6	27.6±1.7
$\Delta S^{\neq}$ (J mol^{-1} K^{-1})	284±4	225±6

[Isoproturon] = 5.0×10^{-5} mol dm^{-3}, [HCl] = 1.0×10^{-1} mol dm^{-3}, [NaLS] = 2.0×10^{-2} mol dm^{-3}, temperature = 70 °C

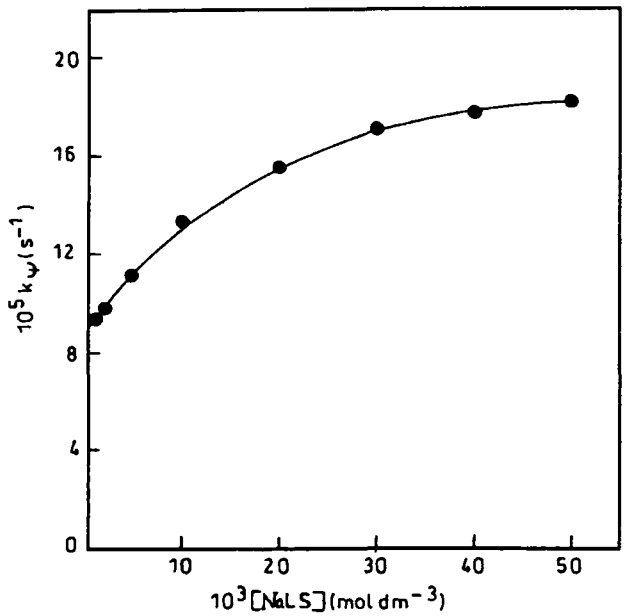


Fig. 2 Effects of surfactant [NaLS] (*filled circle*) on k_ψ. Reaction conditions: isoproturon (5.0×10^{-5} mol dm^{-3}), HCl (1.0×10^{-1} mol dm^{-3}) at 70 °C

The rate equation corresponding to Scheme 2 in terms of pseudo-first-order rate constants is given by

$$k_\psi = \frac{k_w' + k_m' K_s [D_n]}{1 + K_s [D_n]} \tag{1}$$

In this scheme and rate equation, S denotes isoproturon, D_n the micellized surfactant and K_s the binding constant of isoproturon with micelles. Subscripts w and m denote, respectively, the aqueous and the micellar pseudophases. The pseudo-first-order rate constants in aqueous and micellar pseudophases are given by:

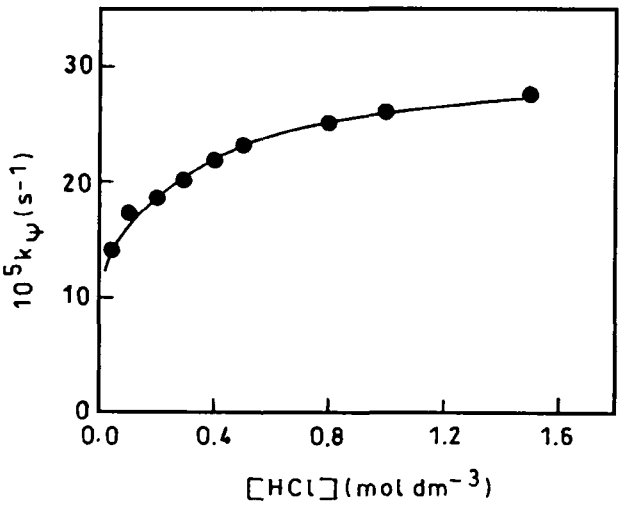
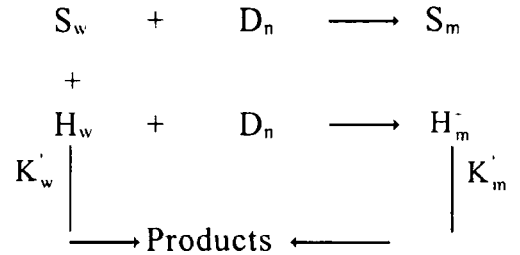


Fig. 3 Effects of [HCl] on the k_ψ. Reaction conditions: isoproturon (5.0×10^{-5} mol dm^{-3}), NaLS (2.0×10^{-2} mol dm^{-3}) at 70 °C



Scheme 2 The reaction occurring in aqueous and micellar pseudophases

$$k_w' = k_w[H^+] \text{ and } k_m' = k_m m_H^s \tag{2}$$

$m_{H^-}^s$ is the molarity of hydrogen ions in micellar pseudophase,

$$m_H^s = [H_m^+]/[D_n] \tag{3}$$

According to the PPIE model, the micellar surface is treated as a selective ion exchanger. The distribution of Na^+ and H^+ in aqueous and micellar pseudophases is given by considering the following equilibrium:

$$H_m^+ + Na_w^+ \overset{K_{H/Na}}{\Leftrightarrow} H_w^+ + Na_m^+ \tag{4}$$

and the equilibrium constant,

$$K_{H/Na} = [Na_m^+][H_w^+]/[Na_w^+][H_m^+]. \tag{5}$$

The reactants exist in dynamic equilibrium between the aqueous and micellar pseudophases. The entrance and exit rates of isoproturon and H^+ from micelles are an order-of-magnitude faster than the rates of its hydrolysis. The distributions of surfactants, substrate, H^+ and counterions Na^+ are at thermodynamic equilibrium throughout the time course of reaction. On applying the mass balance for isoproturon, Na^+, H^+ and surfactant, the following quadratic equation was obtained for m_H^s :

$$m_{H^-}^{s\,2} + \left(\frac{[Na^+] + [H_w^+]}{[D_n]} - \beta\right) m_{H^-}^s - \frac{\beta[H_w^+]}{[D_n]} = 0 \tag{6}$$

where β is the degree of binding of counterion by the micellar surface, and $[H_w^+]$ was obtained from the measured pH (pH = $-\log [H_w^+]$).

Table 2 Parameter used to simulate k_ψ–[NaLS] profile

Parameters	Values
K_s (mol^{-1} dm^3)	410
k_m (mol^{-1} dm^3 s^{-1})	$2.4\pm0.19\times10^{-4}$
β	0.75
$K_{H/Na}$	1.00
CMC (mol dm^{-3})	8.3×10^{-3}

[Isoproturon] = 5×10^{-5} mol dm^{-3}, [HCl] = 1.0×10^{-1} mol dm^{-3}; [NaLS] = 2×10^{-2} mol dm^{-3}, temperature = (70 °C) 343 K

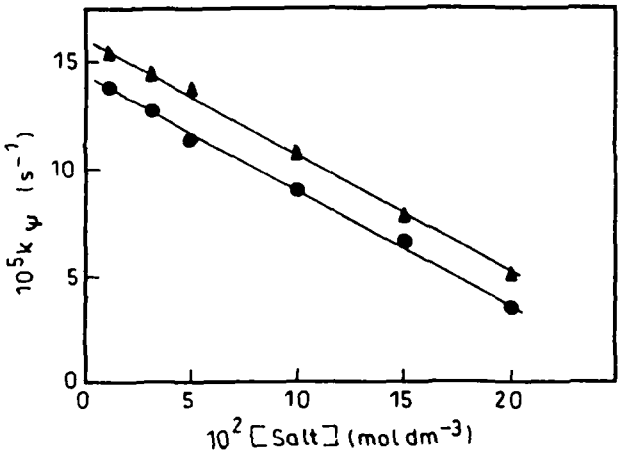


Fig. 4 Effects of [NaCl] (*filled circle*), [KCl] (*filled triangle*) on the k_ψ Reaction conditions: isoproturon (5.0×10^{-5} mol dm^{-3}), NaLS (2.0×10^{-2} mol dm^{-3}) at 70 °C

On substitution of the values of k_m' and k_w' in Eq. 1, the first-order rate equation can be transformed in terms of second-order rate constants as:

$$k_\psi = \frac{k_w[H_f^+] + (k_m K_s - k_w)m_{H^+}^s[D_n]}{1 - K_s[D_n]} \quad (7)$$

where k_m and k_w are second-order rate constants for reactions in micellar and aqueous pseudophases, respectively The fitting values of k_m and K_s were obtained from the computer program by minimizing the deviation between the simulation and the observed values for the k_ψ [NaLS] profile. The values of these parameters are given in Table 2.

The overall increase in the rate of reaction with the increase in NaLS micelles is explained in terms of the binding and concentration of both the reactants, i.e. isoproturon and H^+ within the small vicinity of anionic pseudophase (Stern's layer). The mechanism of the reaction in both the aqueous and micellar pseudophases are similar, as it is evident from the dependence of the rate of reaction on [isoproturon], [HCl] and temperature.

The hydrolysis of isoproturon in acidic media proceeds through an addition elimination mechanism. At low pH, the reaction is initiated by the protonation of carbonyl oxygen, thereby facilitating the nucleophilic attack of water to form tetrahedral intermediate The attack by water molecule is the rate-determining step, and the tetrahedral intermediate decomposes to give phenylcarbamic acid and an amine. Under the acidic condition, the phenylcarbamic acid decarboxylates quickly to yield the final product, i.e 4-isopropyl-aniline (Scheme 1).

The NaLS micelles concentrate both hydrogen ions and isoproturon into a very small volume of Stern's layer. In acidic medium, isoproturon is protonated, and this positively charged isoproturon gets more strongly bonded to anionic NaLS micelles Thus, the micelle facilitates the extensive buildup of protonated isoproturon in the region of Stern's layer and enhances the rate of hydrolysis. In the presence of micelles, the dependence of rate of hydrolysis on [HCl] is linear at lower concentration but shows a levelling behaviour at higher concentration (Fig. 3). The phenomenon may arise due to the low polarity of Stern's layer of micelles as compared to water. The studies by Giffney and O'Connor [15] demonstrate that the rate of hydrolysis of phenylureas increases with the acid strength at low acidity, whereas it passes through a maximum and decreases again in stronger acid solutions. It elaborates the role of water activity during the hydrolysis of phenylureas. The activity of water is reduced appreciably at higher acidic concentrations. The addition of water to the protonated isoproturon (which is the rate-determining step) becomes slow in Stern's layer.

The activation parameters were evaluated from the linear regression of log k_{obs} vs $1/T$ (for aqueous medium) and log k_ψ vs $1/T$ (for surfactant medium) by least-squares method. The values are given in Table 1. The enthalpy and entropy of activation were calculated by using Eyring relationship [18]. The decrease in entropy in the presence of micelles suggests that reactants are in greater degree of orders. The interactions with micelles favour the charge dispersion of reactants in the transition state, and its greater degree of orderliness results in the increases in the values of rate constants.

The added salt (NaCl, KCl) inhibited the reaction, and the values of pseudo-first-order rate constants were decreased (Fig. 4). The inhibition effect could be due to a competitive binding of H^+ and Na^+/K^+ with the micelles [19–21]. The increase in concentrations of Na^+/K^+ causes exclusion of H^+ from the micelles. The added salts also cause micelles to grow and change their shapes from spherical to spheroidal or rod-like. It results into change in reaction rate at micellar surfaces [22–25].

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Kinetics of the Alkaline Hydrolysis of Isoproturon in CTAB and NaLS Micelles

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ABSTRACT Kinetics of the alkaline hydrolysis of isoproturon has been studied in the absence and presence of cetyltrimethylammonium bromide (CTAB) and sodium lauryl sulfate (NaLS) micelles CTAB micelles were found to enhance the rate of reaction while NaLS micelles inhibited the reaction rate The reaction obeyed first-order kinetics in [isoproturon] and was linearly dependent on [NaOH] at lower concentration The rate of reaction became independent at higher [NaOH] At lower [NaOH] the reaction proceeded via formation of hydroxide ion addition complex while at higher [NaOH] the reaction occurred via deprotonation of —NH— leading to the formation of isocyanate The values of k_w k_m and K_s were determined by considering the pseudophase ion exchange model The activation parameters have also been reported The effect of added salts (NaCl and KNO_3) on the reaction rate has also been studied

INTRODUCTION

Phenylureas are widely used in agriculture as active principal ingredients of efficient herbicides They are absorbed by roots and leaves with translocation and act as photosynthetic electron transport inhibitors upon the photosystem II [1] Isoproturon is a selective, systematic herbicide used to control the growth of annual grass and broadleaf weeds in cereals [2,3] The solubility of isoproturon in water is of the order of 10^{-4} mol dm^{-3} Isoproturon is hydrolyzed slowly with the half-life period of 30 days [4] Isoproturon is hydrolyzed in both acidic and alkaline media [5–8] During acidic hydrolysis, the reaction proceeds through the protonation of phenylurea followed by a rate-determining attack by water to yield isopropyl aniline, dimethyl amine, and CO_2 In the alkaline media, Laudien and Mitzner [5] proposed that the reaction occurs via an intermediate hydroxide ion complex formation The attack by water which acts as general acid is the rate determining step The alkaline hydrolysis of phenylureas has also been reported to take place through the formation of isocyanates [8]

Surfactants or detergents are often used in the formulations of pesticides and herbicides [9] because of their poor solubility in water Surfactants spontaneously aggregate at concentrations above the critical micelle concentration (cmc) to form micelles Micelles [10] act as microreactor, which may speed up or inhibit the rates of uni and bimolecular reactions [11–16] Micelles influence the reactivity primarily by binding or excluding reactants and secondarily by changing the free energy of activation [17 18] Aggregate effects on chemical reactivity are generally interpreted by considering micelles and water as separate reaction media or pseudophases

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In the following work, an attempt has been made to systematically study the kinetics of hydrolysis of isoproturon in the micellar media of cationic (cetyltrimethylammonium bromide [CTAB]) and anionic (sodium lauryl sulfate [NaLS]) micelles The influence of these micelles on the rate of reaction has also been explored Rate enhancement in the presence of CTAB micelles has been discussed using the pseudophase ion exchange model, and rate inhibition in the presence of NaLS is explained on the basis of compartmentalization of reactants

EXPERIMENTAL

Materials

Isoproturon, 3-(4-isopropylphenyl)-1,1-dimethylurea (Siris Crop Sciences Limited, New Delhi, India), sodium hydroxide (97%, Merck, India), methanol (99%, Merck, India), sodium chloride (99 9%, Qualigens, India), potassium nitrate (99%, CDH, India), sulfuric acid (98%, Merck, India), CTAB (99%, CDH, India), and NaLS (99%, CDH, India) were used as received All the other salts used were of analytical reagent grade Doubly distilled and deionized water was used throughout the experimental work

Stock solutions of sodium hydroxide (1 0 mol dm^{-3}), CTAB (1×10^{-1} mol dm^{-3}), NaLS (1×10^{-1} mol dm^{-3}), and sulfuric acid (2 mol dm^{-3}) were prepared in doubly distilled water and that of isoproturon (1×10^{-2} mol dm^{-3}) was prepared in methanol

Kinetic Measurements

The requisite amount of surfactant, sodium hydroxide, and methanolic solution of isoproturon was taken in a three-necked reaction vessel The reaction vessel was fitted with a double surface condenser to check any evaporation and was kept in a thermostated water bath at the desired temperature (±0 1 C) The reaction's Q4 progress was followed by measuring the absorbance at constant intervals of time on Elico SL 164 UV–VIS spectrophotometer using 1-cm pathlength quartz cuvettes The hydrolysis reaction was quenched by placing the aliquots in ice cooled water All the kinetic experiments were run under the first order reaction condition in which the concentration of OH^- and surfactant was kept in large excess over isoproturon concentration During basic hydrolysis of isoproturon, the corresponding carbamate was formed with a slightly different value of λ_{max} (248 nm) On addition of a few drops of acid, the carbonyl peak collapsed immediately to give the spectrum of corresponding aniline [19 20] Therefore the absorbance for the extinction of isoproturon was measured by taking 3 mL of aliquots and 1 mL 2 M sulfuric acid at 240 nm wavelength The pseudo-first-order rate constants were determined from the slope of ln $(A - A\alpha)$ vs time, where A is the absorbance of isoproturon at λ_{max} (240 nm) The hydrolytic reaction was followed up to 75% of completion A nonlinear least square technique was used for the treatment of data to obtain the value of K_s and k_m The best values which fit the curves, were obtained from the computer program The cmc of NaLS and CTAB containing isoproturon and sodium hydroxide was determined conductometrically at 70 C, and values were $8\,3 \times 10^{-3}$ mol dm^{-3} and $8\,0 \times 10^{-4}$ mol dm^{-3}, respectively

RESULTS AND DISCUSSION

Reaction in the Aqueous Medium

The hydrolysis of isoproturon substituted both at the phenyl ring and at the nitrogen of the leaving group, was studied kinetically in basic water–methanol solutions (9 1) at 70 C The rate of hydrolysis was determined at different initial concentrations of isoproturon ranging from 4×10^{-5} to $1\,0 \times 10^{-4}$ mol dm^{-3} in 0 1 mol dm^{-3} NaOH at 70 C The values of pseudo first-order rate constants obtained remained the same with the increase in initial concentrations of isoproturon, indicating that the hydrolysis followed first order kinetics with respect to [isoproturon] The dependence of rate of hydrolysis on [NaOH] was deduced from the values of rate constant obtained at several NaOH concentrations ranging from 1×10^{-2} to 1 0 mol dm^{-3} at fixed [isoproturon] (5×10^{-5} mol dm^{-3}) at 70 C (Fig 1) Initially, the rate constant values increased with an increase in [NaOH] but at higher Q5 [NaOH] the increase in rate constant values became almost constant

Kinetic runs were also performed within the temperature range of 40–80 C keeping the concentrations of NaOH and isoproturon constant at 0 1 mol dm^{-3} and $5\,0 \times 10^{-5}$ mol dm^{-3} respectively The energy of activation was determined from the plot of log k_{obs} vs $1/T$ and the values are given in Table I

At lower OH^- concentration, the hydrolysis of isoproturon is presumed to occur through the attack of OH^- on the carbonyl carbon It results in the formation of an intermediate hydroxide ion addition complex [6] Water acting as general acid facilitates the elimination of dimethylamine and leads to the formation of corresponding carbamic acid (Scheme 1)

The reaction follows an addition elimination mechanism, and the rate determining step is the attack of

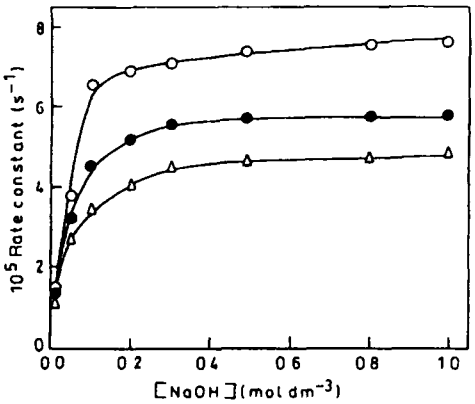


Figure 1 Effect of [NaOH] on the rate constant (k_{obs} for aqueous, k_{ψ} for CTAB and NaLS) in aqueous (●), CTAB (○), and NaLS (Δ) media Reaction conditions [isoproturon] (5.0×10^{-5} mol dm^{-3}), [CTAB] (2.0×10^{-2} mol dm^{-3}) [NaLS] (2.0×10^{-2} mol dm^{-3}) at 70 C

water molecule leading to the formation of carbamic acid Carbamic acid is a stable compound in basic and neutral solutions, but in acidic solution it is very unstable and decomposes rapidly to form corresponding aniline and carbon dioxide

At high OH^- concentration, the hydrolysis proceeds through the fast reversible deprotonation of nitrogen (attached to phenyl group) followed by slow protonation of dimethyl amino nitrogen by water [7] The reaction may be represented by Scheme 2

During hydrolysis at high pH, the intermediate, phenyl isocyanate hydrolyses rapidly to yield phenyl carbamic acid Moodie and coworkers [21] reported a half-life of 20 s for the hydrolysis of phenyl isocyanate in aqueous solution at 25 C Thus under our reaction conditions of [OH^-] (0 1 mol dm^{-3}), it can be safely concluded that the reaction occurs via deprotonation of nitrogen, leading to the formation of the unstable intermediate phenyl isocyanate and finally phenyl carbamic acid The leveling behavior of the rate on [OH^-] profile may be attributed to the rate-determining attack of water on dimethyl nitrogen The activity of water, which acts as general acids, is reduced with the increase in [OH^-], and therefore the rate of hydrolysis becomes independent of [OH^-]

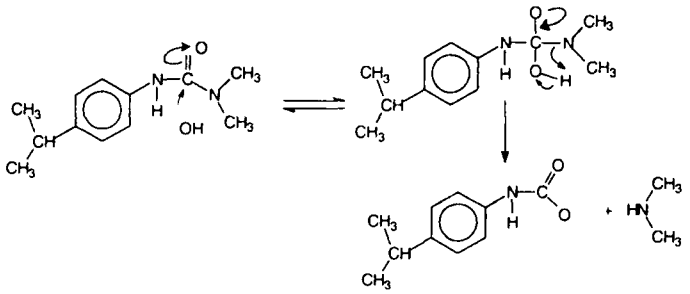
Reaction in the Presence of Cationic (CTAB) and Anionic (NaLS) Micelles

The effect of varying [CTAB] (from 5×10^{-4} to 6×10^{-2} mol dm^{-3}) and [NaLS] (from 5.0×10^{-4} to 6.0×10^{-2} mol dm^{-3}) on the rate of hydrolysis of

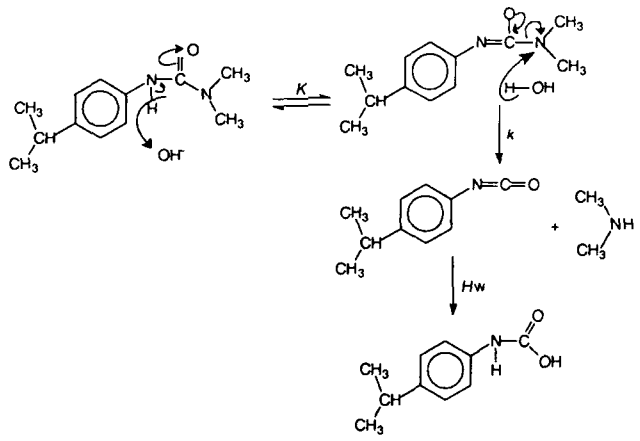
Table I Values of Activation Parameters for the Hydrolysis of Isoproturon by Sodium Hydroxide in the Absence and Presence of Surfactants

		In the Presence of Surfactants	
Activation Parameters	In the Absence of Surfactants	NaLS	CTAB
E_a (kJ mol^{-1})	35 31	24 95	39 01
$\Delta H^{\#}$ (kJ mol^{-1})	32 83	22 47	36 53
$\Delta S^{\#}$ (J k^{-1} mol^{-1})	233 5	266 45	219 56

[Isoproturon] = 5 0 × 10 ^{5} mol dm ^{3} [NaOH] = 0 1 mol dm
[NaLS] = 2 0 × 10 mol dm ^{3} [CTAB] = 2 0 × 10 ^{2} mol dm temperature = 70 C



Scheme 1



Scheme 2

isoproturon was studied at [isoproturon] (5×10^{-5} mol dm^{-3}) in 0 1 mol dm^{-3} NaOH at 70 C Experimental pseudo-first-order rate constant, k_ψ , variation with surfactant concentration showed a sigmoidal behavior in CTAB micelles in which the maximum rate was observed at [CTAB] ($2\,0 \times 10^{-2}$ mol dm^{-3}) The rate decreased with any further increase in [CTAB] A continuous decrease in k_ψ, was observed with [NaLS] for the rate of hydrolysis in NaLS micelles (Fig 2)

The kinetic experiments performed in the presence of cationic CTAB ([CTAB] $= 2\,0 \times 10^{-2}$ mol dm^{-3}) and anionic NaLS ([NaLS] $= 2\,0 \times 10^{-2}$ mol dm^{-3}) micelles showed that the values of k_ψ were independent of the initial concentration of isoproturon and the dependence of k_ψ on [NaOH] was similar to that observed in aqueous medium (Fig 1) The similar behavior observed for variation in rate constants with [isoproturon] and [NaOH] in the absence and presence of surfactants suggest that the reaction followed the same mechanism in aqueous and micellar media The activation parameters were determined by obtaining the values of k_ψ in the temperature range 40–80 C at [isoproturon] ($5\,0 \times 10^{-5}$ mol dm^{-3}) in 0 1 mol dm^{-3} NaOH at a fixed [surfactant] ($2\,0 \times 10^{-2}$ mol dm^{-3}) and are given in Table 1

From the behavior of dependence of rate of hydrolysis of isoproturon on [NaOH] and [isoproturon] in aqueous and micellar media, it is assumed that a similar mechanism was obeyed by the reaction both in micellar and aqueous media The results in the micellar medium can be explained by means of pseudophase kinetic model proposed by Menger and Portnoy [22] and later developed by Bunton and Savelle [17], Romsted [23], and Vera and Rodenas [14] In pseudophase kinetic model, the total volume of micelle is considered as a separated phase uniformly distributed in the aqueous phase and the reaction occurs in both the phases, i e , aqueous and micellar phases

Scheme 3 is therefore, proposed for micellar-catalyzed reaction In this scheme, S denotes isoproturon, D_n the micellized surfactant ($D_n = [\text{total surfactant}] - \text{cmc}$]) and K_s the binding constant ($K_s = [S_m]/[S_w][D_n]$) of isoproturon with micelles Subscripts "w" and "m ' denote aqueous and micellar pseudophases, respectively

The rate is expressed as

$$v = k_\psi[S_T] = k[OH_T^-][S_T] = k_w[S_w] + k_m[S_m]$$

where

$$[S_T] = [S_w] + [S_m]$$

$$[OH_T^-] = [OH_w^-] + [OH_m^-]$$

and

$$k_\psi = \frac{k'_w + k'_m K_s[D_n]}{1 + K_s[D_n]} \qquad (1)$$

The pseudo first order rate constants in aqueous (k'_w) and micellar (k_m) pseudophase are given by

$$k_w = k_w[OH_w^-] \qquad (2)$$

$$k_m = \frac{k_m[OH_m^-]}{D_n} = k_m m_{OH} \qquad (3)$$

where m_{OH} is mole ratio of micellar bound $[OH_m^-]$ to micellar head group

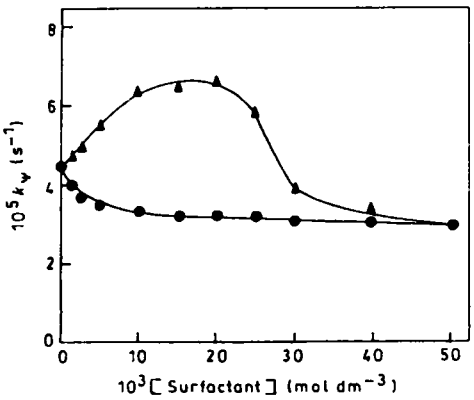


Figure 2 Effect of variation of [surfactant] (CTAB (▲) NaLS (●)) on k_ψ. Reaction conditions [isoproturon] (5.0×10^{-5} mol dm^{-3}), [NaOH] (0.1 mol dm^{-3}) at 70 C

Equation (1) can now be written as

$$k_\psi = \frac{k_w[OH_T^-] + (k_m K_s - k_w) m_{OH^-} [D_n]}{1 + K_s[D_n]} \quad (4)$$

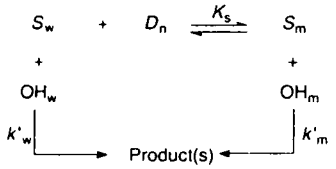
For reaction involving ions, Romsted [23] proposed a theoretical method assuming that ions bind to micelles according to the ion exchange model developed for ion exchange resin

For OH^- reactive ion and Br^- as micelles counter ion, the ion exchange equilibrium can be expressed as

$$OH_m^- + Br_w^- \underset{}{\overset{K_{OH/Br}}{\rightleftharpoons}} OH_w^- + Br_m^- \quad (5)$$

with an equilibrium constant

$$K_{OH/Br} = \frac{[OH_m^-][Br_w^-]}{[OH_w^-][Br_m^-]} \quad (6)$$



Scheme 3

m_{OH^-} in terms of K_{OH}^-/Br^- is expressed as

$$m_{OH^-}^2 + m_{OH^-}\left[\frac{[OH_T^-] + K_{OH^-/Br^-}[Br_T^-]}{(K_{OH^-\ Br^-} - 1)[D_n]} - \beta\right] - \frac{\beta[OH_T^-]}{(K_{OH^-\ Br^-} - 1)[D_n]} = 0 \quad (7)$$

where β is the fraction of neutralized micellar surface (for CTAB $\beta = 0.80$) [24]

The reactant exists in dynamic equilibrium between the aqueous and micellar pseudophase The entrance and exit rate of isoproturon and OH^- from micelles are an order of magnitude higher than the rate of its hydrolysis [25]

The fitting values of k_m, K_{OH}^-/Br^-, and K_s were obtained from the computer program by minimizing the deviation between the simulation and the observed values for k_ψ – [surfactant] profile The values of these parameters are given in Table II

The observed higher rate in CTAB could be attributed to the binding of isoproturon to the positively charged micellar surface The electron-rich carbonyl part of isoproturon is oriented toward the positively charged surface layer of CTAB micelles and the non polar part i e the isopropyl phenyl group is immersed in the micellar core Therefore, the reactive part of isoproturon and OH^- lie in the micellar Stern layer, and the reaction catalyzed by CTAB micelles, occurs in the Stern layer of the micelles With the increase in [CTAB], the local molarities of isoproturon and OH^- ions in the Stern layer are increased, and therefore an enhancement in the rate of reaction is observed

With further increase in [CTAB], the hydrolysis rate decreases and two distinct effects can be considered to explain this phenomenon First the increase in surfactant concentrations results in an increase in the number of unreactive Br^- ions, which replace the micellar

Table II Parameters Used to Simulate k_ψ – [Surfactant] Profile

Parameters	Values	
	NaLS	CTAB
K_s (mol $^{-1}$ dm ^{3})	10.2	240
k_m (mol $^{-1}$ dm ^{3} s^{-1})	–	$1.43 \pm 0.26 \times 10^{-4}$
β	–	0.8
K_{OH^-/Br^-}	–	6.00
cmc (mol dm $^{-3}$)	8.3×10^{-3}	8.0×10^{-4}

[Isoproturon] = 5.0×10^{-5} mol dm $^{-3}$ [NaOH] = 0.1 mol dm $^{-3}$ [NaLS] = 2.0×10^{-2} mol dm $^{-3}$ [CTAB] = 2.0×10^{-3} mol dm $^{-3}$ temperature = 70 C

bound OH^- ions This displacement of OH^- from the vicinity of the Stern layer causes a decrease in $[OH^-]$, therefore, the decrease in the rate of reaction at high surfactant concentrations can be explained by considering the concentration effect of the reaction on, or around, the micellar CTAB Second, the increase in surfactant concentrations causes dilution of OH^- in the micellar pseudophase because of the formation of a large number of micelles

Enhancement of reaction rate by CTAB can thus surface CTAB concentrates both OH^- and isoproturon onto the surface of micelles and brings the reactants in close proximity, thus enhancing the reaction rate

Reaction in the Presence of Anionic NaLS Micelles

A continuous decrease in k_ψ was observed with an increase in [NaLS] at constant [isoproturon] (5.0×10^{-5} mol dm^{-3}) and [NaOH] (0.1 mol dm^{-3}) (Fig. 2). Inhibition of reaction rate is explained by considering the fact that OH^- being anionic does not bind to NaLS micelles in the Stern layer and exists in aqueous medium The deprotonated isoproturon or the negatively charged tetrahedral intermediate is also being repelled by the negatively charged head group of NaLS micelles

Reactions in the presence of NaLS micelles occur mainly in the aqueous pseudophase and k_m and m_{OH} become zero in Eq. (6). Equation (4) is now reduced to

$$k_\psi = \frac{k_w[OH_T^-]}{1 + K_S[D_n]}$$

or

$$\frac{k_w[OH_T^-]}{k_\psi} = 1 + K_S[D_n] \qquad (8)$$

On plotting $k_w[OH_T^-]/k_\psi$ vs $[D_n]$, a straight line was obtained (Fig. 3). The value of the binding constant of isoproturon with NaLS micelles ($K_s = 10.2$) was obtained from the slope of the plot The low value of K_s indicates the weak association between the anionic NaLS micelles and the deprotonated negatively charged isoproturon

The enthalpies of the reactions were evaluated from the linear regression of log k_{obs} vs $1/T$ (for aqueous hydrolysis) and log k_ψ vs $1/T$ (for hydrolysis in the presence of surfactants) by the least square method The energies of activation were calculated by using the Eyring relationship [26]. The difference in enthalpies in the aqueous and micellar media is probably a reflection of the different orientations of the solubilized substrates in the micellar and aqueous media The low variation observed in values of entropies in aqueous and micellar media suggests that there is little change

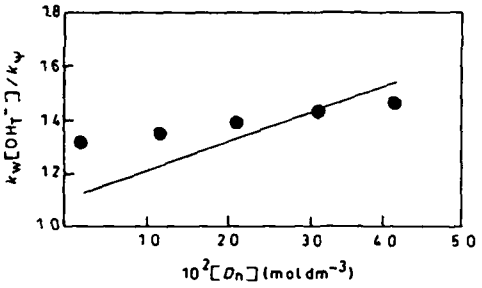


Figure 3 Plot of $k_w[OH_T^-]/k_\psi$ vs $[D_n]$. Reaction conditions [isoproturon] (5.0×10^{-5} mol dm^{-3}), [NaOH] (0.1 mol dm^{-3}) at 70 C

in orderliness during the whole course of the reaction, i.e., from the attack of OH^- or the deprotonation of —NH— to the formation of a transition state to finally the product

Inhibition of Rate of Hydrolysis by Salts

Figure 4 shows the effect of increasing [NaCl] and $[KNO_3]$ on the interaction between isoproturon and NaOH in the presence of CTAB and NaLS micelles The addition of NaCl decreased the rate of reaction, while the addition of KNO_3 had a less inhibiting effect Inhibition of catalysis by the addition of salt could be due to competitive binding of counterions present with the micelles [27–29].

The addition of salt decreases the concentration of OH^- in the Stern layer and thereby decreases the rate The inhibition of the micellar-catalyzed reaction may also be due to the presence of salts, which increase the aggregation number An increase in aggregation number reduces the catalytic efficiency of the surfactants

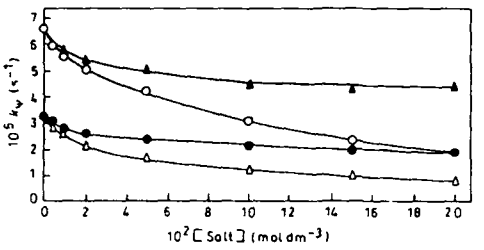


Figure 4 Effect of variation of [NaCl] and $[KNO_3]$ on the K_ψ (▲ ○) for KNO_3 and NaCl, respectively, at [CTAB] (2.0×10^{-2} mol dm^{-3}) (● △) for KNO_3 and NaCl, respectively at [NaLS] (2.0×10^{-2} mol dm^{-3}). Reaction conditions [isoproturon] (5.0×10^{-5} mol dm^{-3}) [NaOH] (0.1 mol dm^{-3}) at 70 C

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